

Photobiodegradation of Low-Density Polyethylene/Banana Starch Films

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ABSTRACT: The effects of the starch content, photosensitizer content, and compatibilizer on the photobiodegradability of low-density polyethylene (LDPE) and banana starch polymer blend films were investigated. The compatibilizer and photosensitizer used in the films were PE-*graft*-maleic anhydride (PE-*g*-MA) and benzophenone, respectively. Dried banana starch at 0–20% (w/w) of LDPE, benzophenone at 0–1% (w/w) of LDPE, and PE-*g*-MA at 10% (w/w) of banana starch were added to LDPE. The photodegradation of the blend films was performed with outdoor exposure. The progress of the photodegradation was followed by determining the carbonyl index derived from Fourier transform IR measurements and the changes in tensile properties. Biodegradation of the blend films was investigated by a soil burial test. The biodegradation process was followed by

measuring the changes in the physical appearance, weight loss, and tensile properties of the films. The results showed that both photo- and biodegradation rates increased with increasing amounts of banana starch, whereas the tensile properties of the films decreased. The blends with higher amounts of benzophenone showed higher rates of photodegradation, although their biodegradation rates were reduced with an increase in benzophenone content. The addition of PE-*g*-MA into polymer blends led to an increase in the tensile properties whereas the photobiodegradation was slightly decreased compared to the films without PE-*g*-MA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2725–2736, 2006

Key words: polyethylene; biodegradable; blends; banana starch; polyethylene-*graft*-maleic anhydride

INTRODUCTION

Plastic waste is now regarded as a worldwide environmental problem. The disposal of plastics, especially those used in packaging, poses a serious challenge to waste management. This is because such materials tend to accumulate in nature because of their excellent mechanical properties, as well as chemical, weather, and biodegradable resistance.

The solution to reduce the problems of plastic waste management is the production and use of environmentally friendly degradable polymers, especially those used in packaging applications.

Generally, biodegradation of synthetic polymers involves enzymatic and chemical degradation by living microorganisms. The primary mechanism for the enzymatic degradation of polymers takes place by hydrolysis and oxidation.¹ Most synthetic polymers cannot be degraded by microorganisms. To increase their biodegradability, nonbiodegradable polymers are associated with natural biopolymers such as starch, cellulose, lignin, and dextrin. Adding these additives to synthetic polymers increases the polymer chain oxidation reaction. Natural polymers are susceptible to mi-

crobial attack. This leads to physical embrittlement of the polymers, leaving porous and mechanically weakened polymers. The microbes in turn release non-specific oxidative enzymes that could attack the synthetic polymers. In addition, the gradual degradation of natural polymers leads to increased surface area by erosion and pitting. This accelerates degradation of the synthetic polymers by diffusion of oxygen, moisture, and enzymes into the porous polymer matrix.^{2–4}

Starch, which is a mixture of amylose and amylopectin, is a renewable and fully biodegradable polymer that is readily available in high purity and at low cost. It has drawn a lot of attention in the preparation of biodegradable plastics. The addition of starch to synthetic plastics like polypropylene,^{5,6} poly(vinyl alcohol),⁷ high-density polyethylene (PE),^{8,9} linear low-density PE,^{10,11} and low-density PE (LDPE)^{2,3,12–17} has reportedly enhanced their biodegradability.

Banana is likely the most popular tropical fruit in Thailand. All parts of the plant can be used. The fruit is highly versatile in terms of how to eat it. It is rich in starch content (14–23% on a fresh weight basis or 61–76% on a dry weight basis).¹⁸ However, bananas ripen easily. They begin to ripen as soon as they are harvested. To improve the added value of raw materials in the country, starch extracted from bananas is an interesting choice to use as a filler in polymers. Many researchers have studied starch from bananas;

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however, those works have focused only on the composition, physical, and chemical properties of banana starch in order to use it in the food industry.^{18–22}

The degradation of synthetic plastics in nature involves environmental factors. For example, polymers discarded as packaging litter end up in the outdoor environment and are in contact with soil and exposed to sunlight. In this case, improvement of both the photo- and biodegradability of polymers offers the best solution.

UV radiation or sunlight has been recognized as an important factor in the aging and weathering deterioration process that occurs in commercial polymers. PE is relatively resistant to UV radiation in the absence of oxygen. However, when it is exposed to both oxygen and UV radiation, it becomes brittle because of photooxidation. Hydroperoxide and carbonyl groups are generated and then PE molecules that contain carbonyl groups dissociate by Norrish type I or type II reactions.^{23,24} These processes result in a reduction in the polymer molecular weight.

The photodegradation of plastics can be enhanced by two basic routes. The first one is the introduction of a chromophoric group in the backbone of the polymeric chain during or after the polymerization process in comonomer form. Chromophoric groups are necessary to absorb incident radiation. In polymers, these are usually unsaturated structures such as carbonyl, ethylenic, or aromatic groups. These chromophores can give rise to the initiation of new chain reactions upon prolonged irradiation and thus to rapid deterioration of the polymers. The second route is adding or mixing low molecular weight chemicals, so-called photosensitizers, in the form of additives.^{23,24}

Many studies have been carried out to achieve the promotion of degradation of synthetic polymers such as PE by the addition of a photosensitizer. The examples of a photosensitizer are aromatic carbonyl compounds, such as benzophenone, and quinones, such as anthraquinone.²³ The effect of organic metal compound photosensitizers, such as iron complexes,²⁵ manganese complexes,²⁶ ferric stearate,^{27,28} and ferric dithiocarbamate²⁹, in promoting the photodegradation of polymers has also been reported. In addition, inorganic metal oxides and salts (e.g., ZnO, TiO₂,^{28,30} and FeCl₃) can accelerate photodegradation as well.

In this work, an attempt was made to obtain a photobiodegradable polymer film by incorporating banana starch and photosensitizer into LDPE. Benzophenone and PE-*graft*-maleic anhydride copolymer (PE-*g*-MA) were studied as a photosensitizer and a compatibilizer, respectively. The amount of banana starch and photosensitizer were varied from 0 to 20 and 0 to 1 wt %, respectively. The biodegradation of LDPE blend films was assessed by a soil burial test and the photodegradation was estimated by an outdoor exposure test. The effects of the compatibilizer,

banana starch content, and photosensitizer content on the degradation behavior were followed by observing the changes in the physical appearance, weight loss, tensile properties, and carbonyl index of the films.

EXPERIMENTAL

Materials

Extrusion film grade LDPE (LD1902F) was obtained from Cementhai Commercial Co., Ltd. Its melt flow index and density were 2.0 g/10 min and 0.919 g/cm³, respectively. Benzophenone was purchased from A.C.S. Xenon Limited Partnership. PE-*g*-MA copolymer with 0.5–1 wt % grafting level was kindly supplied by Dupont Co., Ltd. under trade name Fusabond. Banana starch (*Musa sapientum* Linn.) was used as a biodegradable additive. The preparation of banana starch was described elsewhere.³¹

Film preparation

A Thermoprism twin-screw extruder (model DSR-28) was used to mix the blend composition. Prior to mixing, the banana starch was dried in an air oven at 80°C for 24 h. The constituents (LDPE, banana starch, benzophenone, and PE-*g*-MA) were physically premixed before being fed into the extruder. The temperature profile of the five zone extruder was 100, 135, 140, 145, and 150°C. The screw speed was kept constant at 25 rpm. The banana starch content was 5, 10, 15, and 20 wt % whereas the benzophenone concentration was varied in three different levels (0.25, 0.50, and 1.0 wt %). The amount of starch and photosensitizer was varied based on the LDPE content. In these blends, PE-*g*-MA was used as a compatibilizer at 10 wt % based on the banana starch content. After mixing, the extrudate was cooled, pelletized, and dried. Finally, the starch-based LDPE films were prepared using a Collin chill roll cast film (model ECS-T10). The barrel temperature was 100–160°C, and the screw speed was 25 rpm.

Photodegradation process

Outdoor exposure of LDPE films with various amounts of banana starch and benzophenone was carried out in Bangkok, Thailand, for 4 months. The natural exposure was from September to December, 2003. The film samples were cut into rectangular shapes (25 × 30 cm) and then fixed on the exposure racks with a 45° angle to the horizontal (Fig. 1). The racks were designed in accordance with ASTM D 1435-94. The tensile properties and carbonyl index of the film samples were tested each month of the exposure time. The weathering climate data during 4

months of exposure were received from the Meteorological Department and are summarized in Table I.

Biodegradation process

The biodegradation of the film samples was followed during soil burial for 4 months. The films were cut into 1.5×20 cm pieces. Soil was placed into a plastic box ($35 \times 45 \times 35$ cm) with tiny holes at the bottom and on each sides of the box to increase air and water circulation. The soil was kept moist with water and stored outside the room at ambient humidity (71–77%) and temperature (26–30°C). Samples were buried in the soil at a depth of 30 cm from the surface. The rate of biodegradation was followed by measuring the percentage weight loss, tensile properties, and physical appearance of the film samples each month in the soil. Prior to measuring, samples were washed with distilled water and dried under a vacuum oven at 60°C for 24 h.

Degradation assessment

Carbonyl index

The carbonyl group evolution was measured by Fourier transform IR (FTIR, Nicolet model Impact 400D). The film samples were scanned at a frequency range of $4000\text{--}400\text{ cm}^{-1}$. A carbonyl index (CI), which is defined as the ratio of the absorbance (A) at two different wavenumbers, is calculated according to eq. (1):

$$CI = A_{1715} / A_{1467} \quad (1)$$

Tensile properties

Tensile tests of rectangular film specimens ($1.5\text{ cm} \times 20\text{ cm} \times \sim 100\ \mu\text{m}$, width \times length \times thickness)



Figure 1 The exposure racks for the outdoor exposure study. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Data of Thailand Weathering Climate at Bangkok Metropolis in 2003

Month	Temp. (°C)	RH (%)	Rainfall amount (mm)	Radiation (MJ/m ²)
September	28.7	77	197.6	472.67
October	28.6	76	346.6	433.98
November	28.3	73	135.9	516.53
December	28.7	71	54.1	502.03

were conducted using a universal testing machine (LLOYD LR 100K) at a crosshead speed of 50 mm/min and a gauge length of 10 cm, according to ASTM D 882. At least five specimens of each film were tested.

Physical appearance

A scanning electron microscope (JEOL JSM-5410LV) was used to investigate the morphology of the film samples. Each sample was washed with distilled water and dried in a vacuum oven at 60°C for 24 h. The scanning electron microscope was operated at 15 kV. The films surface were sputter coated with gold prior to investigation to avoid surface charging under the electron beam.

Weight loss

The weight loss of the films was determined by weighing the sample before and after biodegradation in soil. The percentage weight loss of the film samples was calculated using the following equation:

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (2)$$

where W_i is the initial weight of the sample before degradation (g) and W_f is the final weight of the sample after degradation (g).

RESULTS AND DISCUSSION

Evaluation of photodegradation

The photodegradation rate was evaluated by observing the changes in the chemical structure and tensile properties of the films. Structure changes such as the oxidation level of LDPE due to UV sunlight can be accurately detected by FTIR. The carbonyl indexes of the LDPE blend films were calculated to obtain quantitative information of the structure changes.

Effect of starch content

Figure 2 illustrates the carbonyl index of LDPE/banana starch films without PE-g-MA and benzophenone as a function of time. The data show that, as the exposure time and starch content increased, the carbonyl index increased. This is attributable to the microstructure of the starch granules that are embedded within the LDPE matrix. Our previous results revealed that there is a gap between the banana starch granules and the LDPE matrix.³¹ Therefore, the higher starch content led to an increase in porosity of the LDPE matrix, which then easily allowed the permeation of light and oxygen throughout the inner part of the LDPE, resulting in the higher carbonyl index.

The tensile properties of pure LDPE and LDPE/banana starch films decreased with the exposure time, as seen in Figure 3. As expected, the increase in starch content decreased the tensile properties as a function of time as well. In fact, such a decrease was observed in the tensile strength and elongation at break. For the LDPE film with 20 wt % starch, its tensile strength and elongation at break decreased 46.5 and 99%, respectively, after 4 months of outdoor exposure. However, we found that the reduction rate in the tensile properties of pure LDPE film was greater than that of the composite films. Because of the higher amount of LDPE in the film, which is the part that reacts directly to sunlight, the LDPE film showed 48 and 150% reductions in tensile strength and elongation at break, respectively.

Effect of compatibilizer

Figure 4 shows the influence of a compatibilizer on the change of the carbonyl index as a function of the exposure time. For the films containing 10% banana

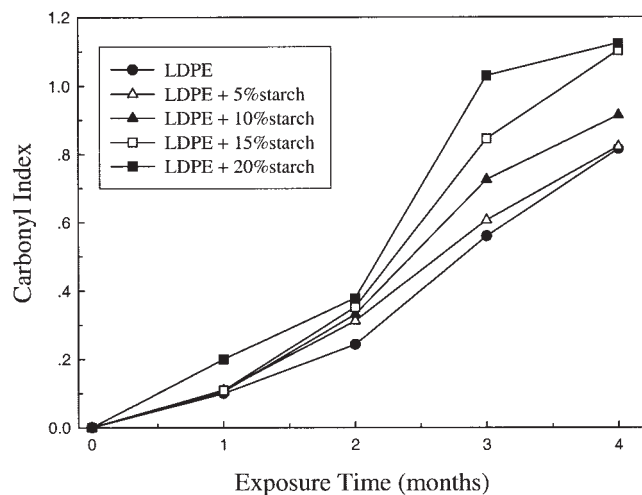
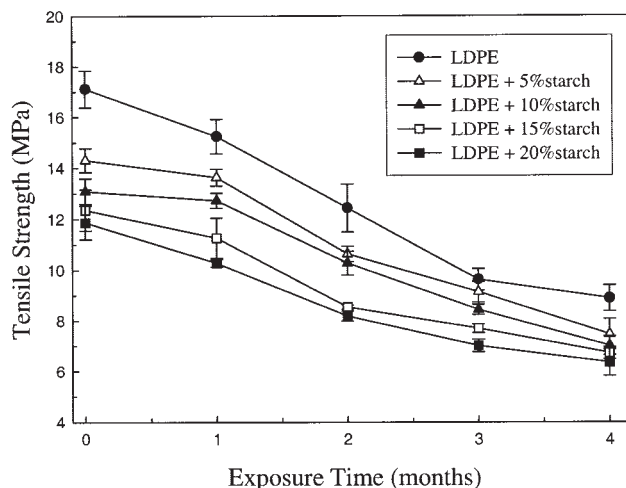
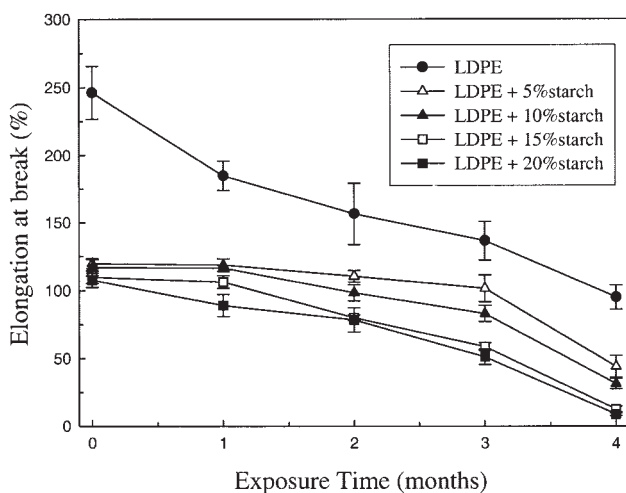


Figure 2 The carbonyl index of LDPE/banana starch films without PE-g-MA and benzophenone.



(a)

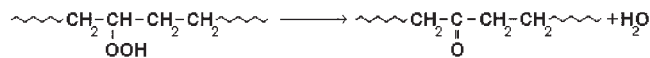


(b)

Figure 3 The (a) tensile strength and (b) elongation at break of LDPE/banana starch films without PE-g-MA and benzophenone.

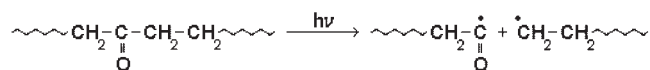
starch, the carbonyl index increased as a function of the exposure time for both compatibilized and uncompatibilized films. Nevertheless, the film containing PE-g-MA did not show any significant difference in the carbonyl index compared to the uncompatibilized film.

Figure 5 shows the plots of the tensile strength and elongation at break of the uncompatibilized and compatibilized film with 10% PE-g-MA as a function of the exposure time. Consistent with the film before being subjected to sunlight, the compatibilized films also exhibited a greater tensile strength compared to the uncompatibilized ones. However, as the exposure time increased, the tensile strength of both compatibilized and uncompatibilized films decreased continuously. The trend was identical to that of the elongation at break. The decrease in the elongation at break was drastic at the last stage. Because the starch granules of

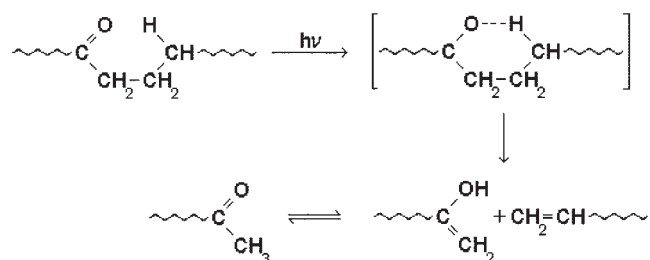


6. Then, the LDPE molecule with the carbonyl group decomposes by a Norrish type I or type II process^{23,24}:

Norrish type I



Norrish type II



Thus, as clearly seen from the above mechanism, the increase in the carbonyl index in LDPE chains resulted from the increase in the amount of small fragments of LDPE chains with carbonyl groups. This mechanism makes the polymer chains shorten and simultaneously decreases the molecular weight and tensile properties of the polymer. The results have the same trend as those reported by Angulo-Sanchez and coworkers.³⁰ In their work, the carbonyl index of the LDPE film containing 4.0 mmol/100 g PE titanium(IV) oxide acetylacetonate was found to be greater than LDPE film containing 1.0 mmol/100 g PE titanium(IV) oxide acetylacetonate. After 60 h of accelerated exposure with a fluorescent lamp, the carbonyl indexes of LDPE with 1.0 mmol/100 g PE titanium(IV) oxide acetylac-

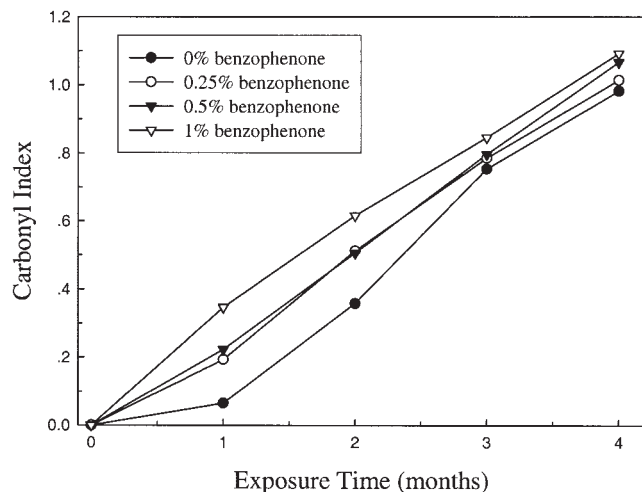
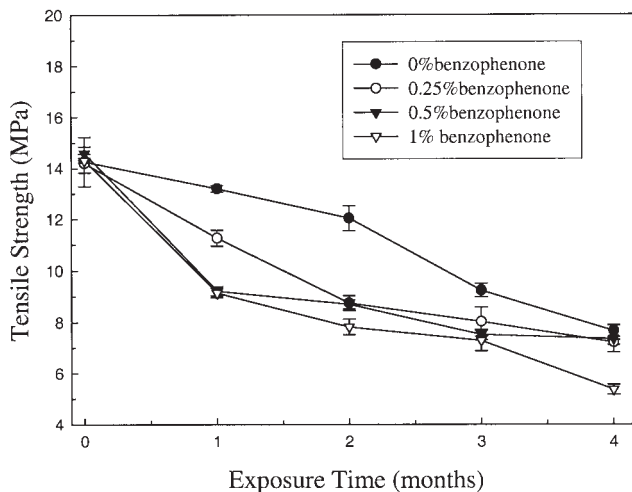
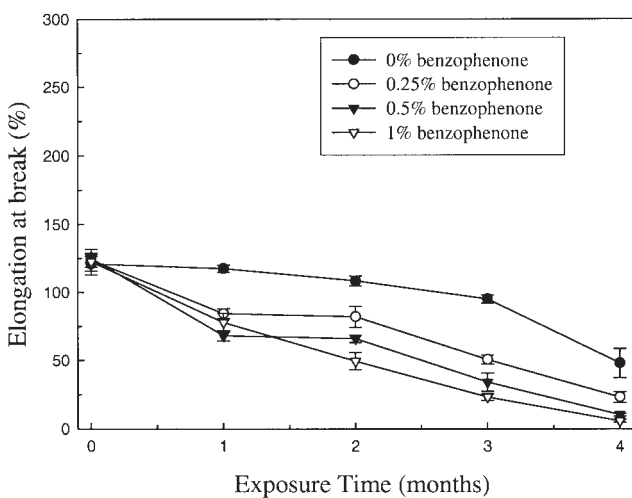


Figure 6 The carbonyl index of LDPE/10% banana starch/10% PE-g-MA films with different amounts of benzophenone.



(a)



(b)

Figure 7 The (a) tensile strength and (b) elongation at break of LDPE/10% banana starch/10% PE-g-MA films with various contents of benzophenone during outdoor exposure tests.

etionate and LDPE with 4.0 mmol/100 g PE titanium(IV) oxide acetylacetonate were 0.86 and 1.14, respectively. Similarly, these results indicated that a higher concentration of photosensitizer was more effective.

The tensile properties of the films containing different contents of benzophenone as a function of time are displayed in Figure 7. The tensile strength and elongation at break of the films decreased with increasing exposure time. In addition, the increase in benzophenone concentration decreased the tensile properties as a function of time as well. The reductions in both the tensile strength and elongation at break with increasing exposure time and benzophenone content are due to chain scission reactions occurring during exposure. As mentioned earlier, benzophenone can generate free

radicals and break down the long polymer chains into shorter ones. As a result, the lowest tensile strength and elongation at break were obtained from the film with 1% benzophenone. Clearly, as seen in Figure 7, its elongation at break was almost zero for the films containing 0.5–1% benzophenone at 4 months of exposure. Similarly, the tensile strength of the film containing 1% benzophenone drastically dropped about 62.5% after being exposed for 4 months. These results mean that, after a certain period of exposure, the film containing some amount of photosensitizer started losing its strength and became brittle.

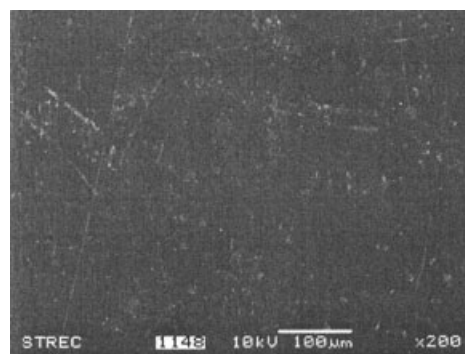
Evaluation of biodegradation

After being subjected to the soil, samples were removed for testing every month. The physical appearance of the film surface was observed by scanning electron microscopy (SEM). In addition, the biodegradation rate was evaluated by measuring the weight loss and tensile properties of the films.

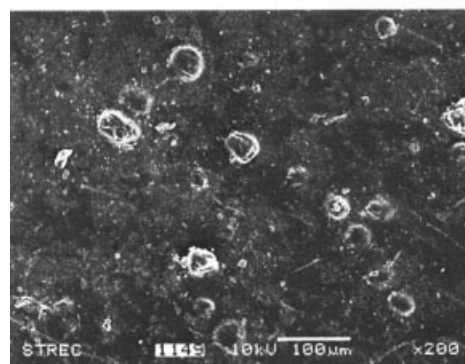
Effect of starch content

The SEM micrographs for LDPE/banana starch films containing different amounts of starch are shown in Figure 8. After 3 months of exposure, there was no indication of biodegradation for pure LDPE film. However, the films with 5 and 20 wt % starch were obviously degraded as evidenced by the existence of small holes on the surface of the films, particularly for the film containing 20 wt % starch. The tiny holes that appeared on the surface of the films confirmed starch removal. This is because there are more sites on the film surface that can be attacked by microorganisms. These SEM micrographs prove that starch is the main carbon source for microorganisms while the LDPE matrix remains unaffected. Therefore, oxygen can attack the newly generated surface with the formation of peroxides and hydroperoxides. These radicals promote scission of the LDPE main chain into small fragments, which are more susceptible to attack by microorganisms. As expected, there were more minute holes when the starch content was increased. These results were confirmed by weight loss measurements.

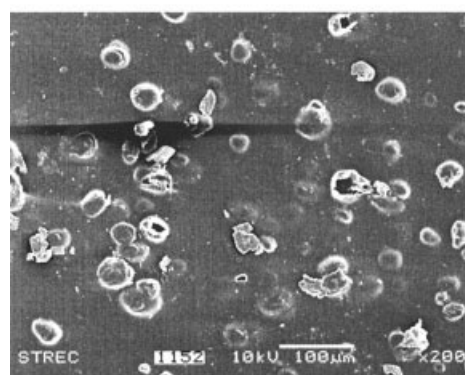
Figure 9 illustrates the weight loss of LDPE and its blends with various amounts of banana starch as a function of the exposure time in soil. As can be observed, starch consumption by microorganisms resulted in weight loss of the blends. LDPE exposed in soil for 4 months did not show any significant weight loss (approximately 0.02%), whereas its blends with starch exhibited greater weight loss. For the blends containing 5 and 10 wt % starch, the amount of starch consumption was insignificant because the weight loss was very small (up to 1%), even after 4 months of exposure. The biodegradation rate rapidly increased



(a)



(b)



(c)

Figure 8 SEM micrographs of (a) pure LDPE and LDPE blends with (b) 5% banana starch and (c) 20% banana starch after 3 months of exposure in soil.

for the blend with 20 wt % starch, even after the first month of exposure.

It was conclusive that the percentage of weight loss increased with the duration of the time of exposure in the soil as well as the starch content. For the blends with higher starch content, starch was more exposed; as a result, a greater portion of it was consumed by microorganisms. In contrast, for the blends containing a lower amount of starch, the starch was almost com-

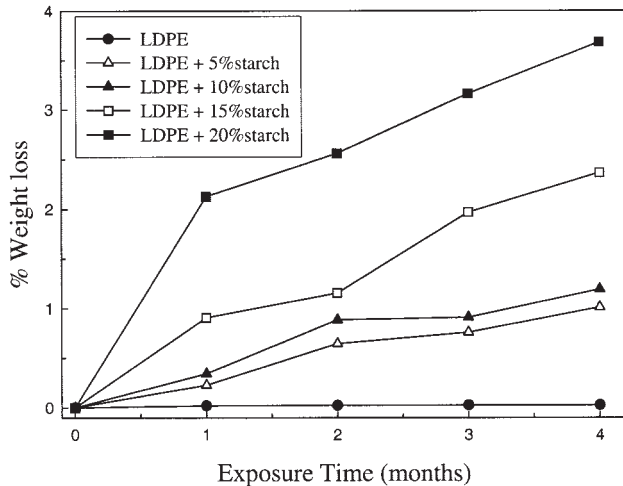


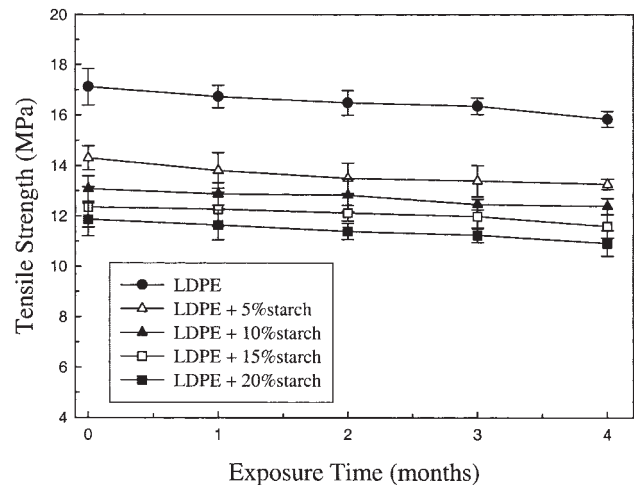
Figure 9 The weight loss of LDPE/banana starch films during the 4-month soil burial test.

pletely covered by LDPE and was not accessible by microorganisms. Because the starch diameter was about one-fourth of the film thickness,³¹ the microorganisms consumed only the starch that was located on the surface of the film.

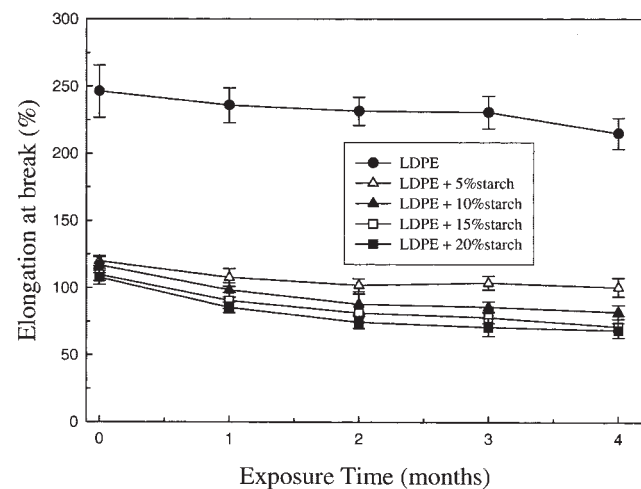
Figure 10 exhibits the tensile properties of LDPE/starch films during soil burial tests. As shown, there was a slight reduction in the tensile strength as the exposure time increased. In addition, increasing the starch content reduced the tensile strength as a function of time as well. For example, after 4 months, the tensile strength and elongation at break of LDPE film decreased by 7.5 and 31.4%, respectively, whereas the introduction of the first 5 wt % starch to LDPE led to a 22.5% decrease in the tensile strength and a 145.8% decrease in the elongation at break. Similar to the weight loss, the reduction in tensile properties during the biodegradation process depended on the exposure time and starch concentration. The reason for this reduction is the starch consumption by microorganisms. Starch consumption results in the destruction of the adhesion between the two phases and creates a large number of cavities in the LDPE matrix. This decrease can also be associated with the lack of compatibility between the two components and with the hydrophilic and hydrophobic characters of starch and LDPE, respectively. These changes are reflected in the tensile properties of the blend films. In comparison with the photodegradation test by outdoor exposure demonstrated in Figure 3, the decrease in tensile properties as a function of exposure time and starch content was more distinct than in the case of the soil burial test. Obviously, after 4 months of outdoor exposure, the tensile strength of the LDPE and LDPE/starch films decreased to about 45.6–48.1%, whereas those of the films buried in the soil decreased only 6.2–8%.

Effect of compatibilizer

Figure 11 provides a comparison of the compatibilized and uncompatibilized films. As seen in Figure 11(a), starch consumption cannot be detected. In contrast, the uncompatibilized blend showed many tiny holes [Fig. 11(b)]. The difference between the uncompatibilized and compatibilized films can be clarified by the following reasons. For uncompatibilized films, the LDPE matrix only encapsulates the starch granules without any bonding. Thus, there is a gap between the LDPE matrix and starch granules. This gap increases the porosity of the LDPE matrix, which can then easily permit the microorganisms to attack throughout the LDPE matrix. For the LDPE/starch film with compatibilizer, the interfacial adhesion between the two components makes the removal of starch granules from the films more difficult. These results are in good

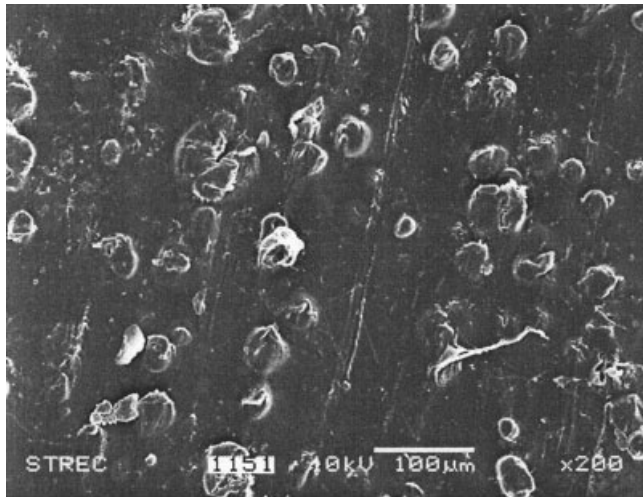


(a)

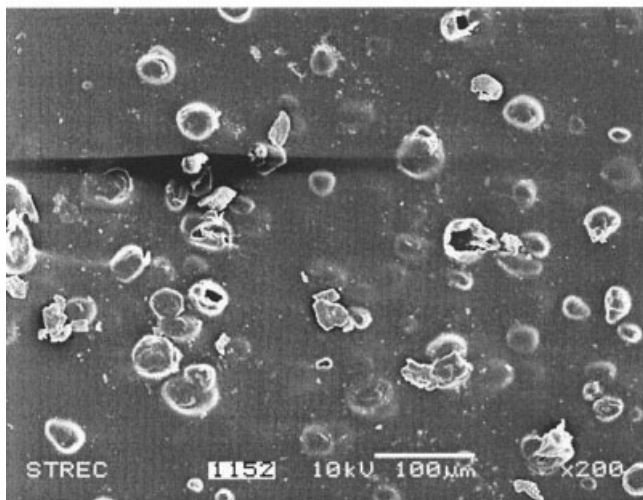


(b)

Figure 10 The (a) tensile strength and (b) elongation at break of LDPE/banana starch films during the 4-month soil burial test.



(a)



(b)

Figure 11 SEM micrographs of LDPE/20% banana starch films after soil burial for 3 months: (a) compatibilized blend with 10% PE-g-MA and (b) uncompatibilized blend.

agreement with the tensile properties that will be discussed shortly.

Figure 12 displays the weight loss of the compatibilized films. Compared to Figure 9, the same behavior was observed in the compatibilized films. The blend with 20% starch showed a significant weight loss compared to the others. To clarify the effect of the compatibilizer (PE-g-MA) on the weight loss of the films, a comparison between compatibilized and uncompatibilized films is shown in Figure 13. This plot suggests that the degradation rate of the compatibilized films was slightly lower than that of the corresponding uncompatibilized one. It might be implied that the compatibilizer has an inhibiting effect on the biodegradation of the film. This PE-g-MA effect may

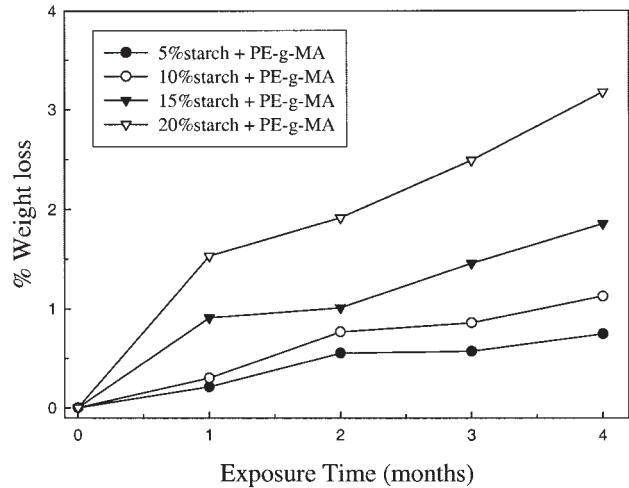


Figure 12 The weight loss of LDPE films with different amounts of banana starch and 10% PE-g-MA.

be due to the bonding between the anhydride groups of the PE-g-MA and the hydroxyl groups of banana starch, which presents or obstructs the consumption of starch from microorganisms in the soil.

Figure 14 shows the tensile strength and elongation at break of the compatibilized and uncompatibilized films. As the exposure time increased, the tensile strength and elongation at break of the compatibilized and uncompatibilized films decreased slowly. However, the compatibilized film with 10% PE-g-MA exhibited slightly greater tensile properties compared to the uncompatibilized ones. After 4 months, the elongation at break of the LDPE/10% banana starch film without PE-g-MA decreased about 38% whereas that of the compatibilized film decreased 28.2% compared to the unexposed films. This is because the starch

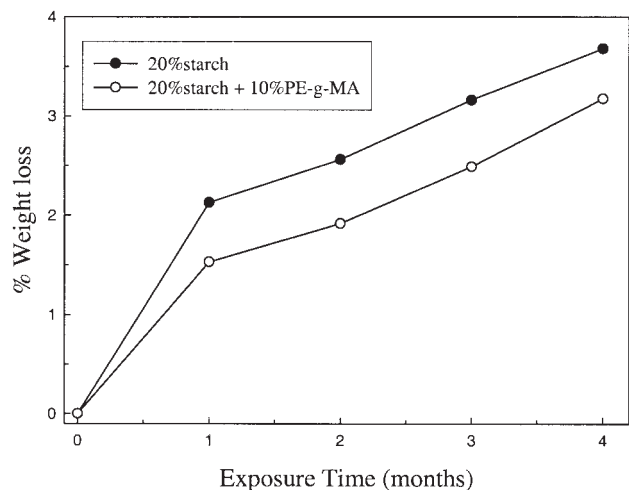
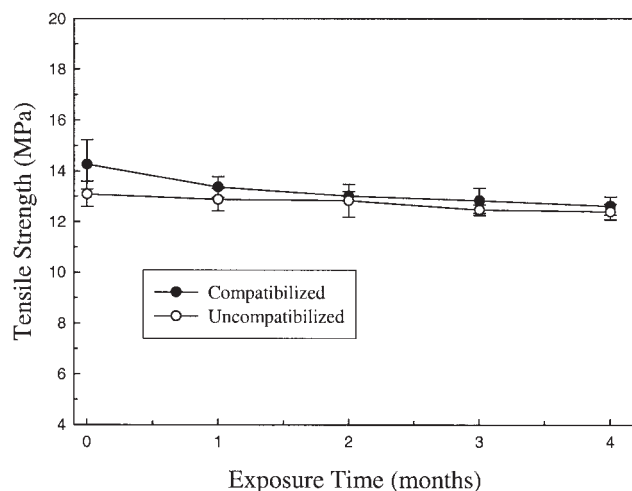


Figure 13 A comparison between LDPE/20% banana starch films with and without 10% PE-g-MA as a compatibilizer.

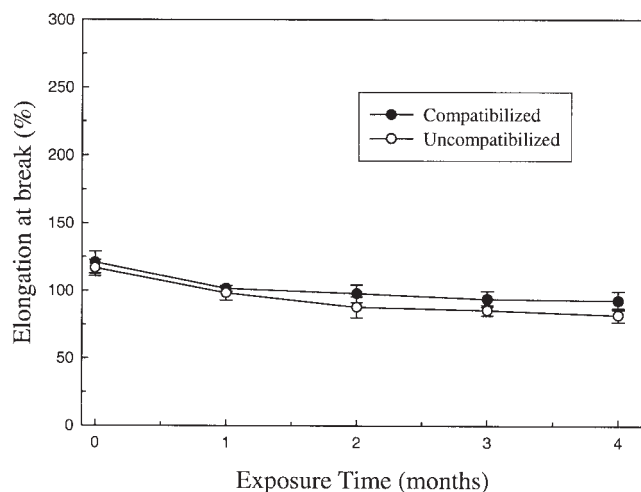
granules of the uncompatibilized film have no interfacial adhesion with the LDPE matrix with respect to the compatibilized film. The uncompatibilized film has more surface areas to be attacked by microorganisms; therefore, it has more microscopic holes randomly scattered in the film than the compatibilized film. Consequently, the tensile properties of the uncompatibilized film were lower than those of the compatibilized film.

Effect of photosensitizer

As shown in Figure 15, it is very difficult to distinguish the difference between LDPE/banana starch films with and without 1% benzophenone. After 3 months of exposure in soil, the result showed that

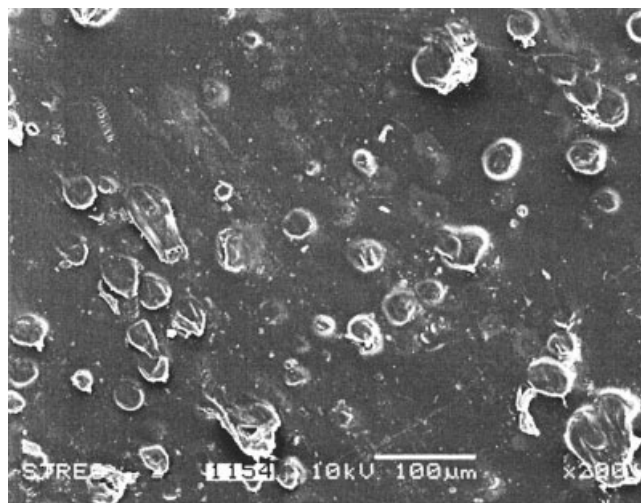


(a)

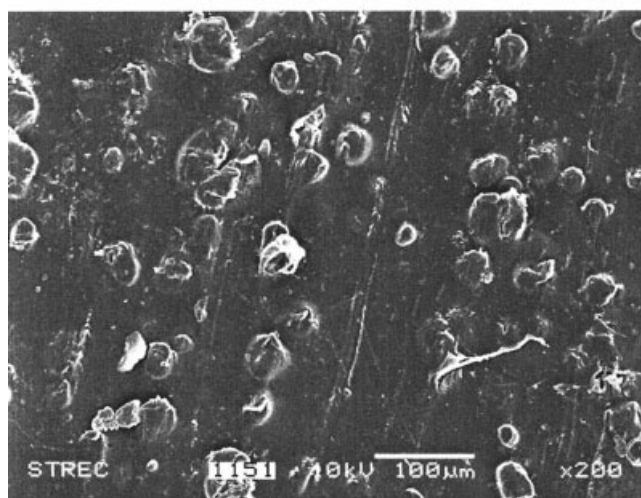


(b)

Figure 14 The (a) tensile strength and (b) elongation at break of LDPE/10% banana starch films uncompatibilized and compatibilized with 10% PE-g-MA during the soil burial test.



(a)



(b)

Figure 15 SEM micrographs of LDPE/20% banana starch/10% PE-g-MA films (a) with 1% benzophenone and (b) without benzophenone after 3 months of exposure in soil.

there were very few small cavities in both of the films. This is because of the presence of the compatibilizer and photosensitizer. Benzophenone is an aromatic carbonyl compound photosensitizer that might be sufficiently toxic to inhibit microbial growth in culture.

The effect of the photosensitizer on the weight loss of the LDPE/banana starch blends as a function of exposure time can be seen in Figure 16. Clearly, the data show that, as the amount of benzophenone increased, the weight loss of the films decreased. This result is similar to the case of the PE-g-MA compatibilizer, in that both PE-g-MA and benzophenone act as an inhibitor and reduce the effectiveness of the biodegradability of the blend films. As clearly depicted in Figure 17, without these two components, the weight

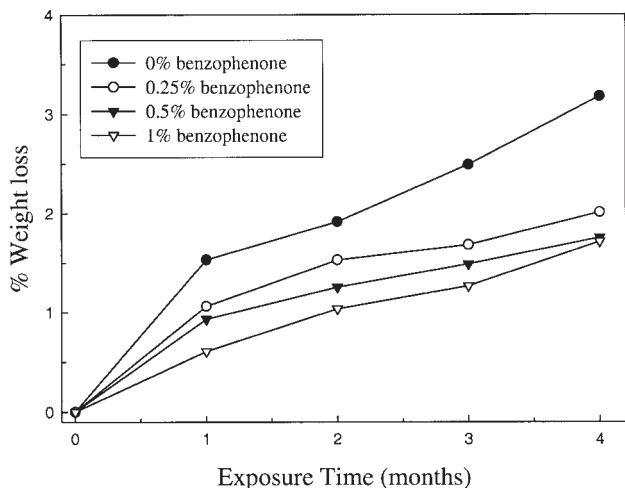
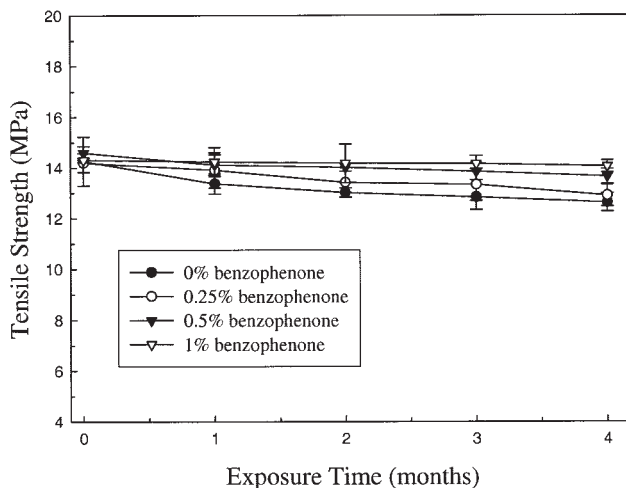


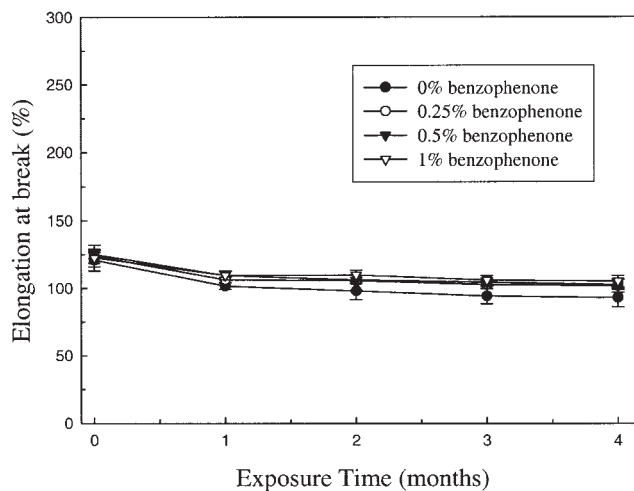
Figure 16 The weight loss of the LDPE/20% banana starch/10% PE-g-MA films with different amounts of photosensitizer.

loss of the LDPE/starch film can be as high as 3.7% after 4 months of exposure. However, the addition of 10% PE-g-MA reduced the weight loss of the blend film to 3.2%. Likewise, the weight loss of the blend film further decreased to 1.7% after adding 1% benzophenone.

Figure 18 displays the plots of the tensile strength and elongation at break as a function of time and photosensitizer content. The tensile properties of all films slightly decreased upon increasing burial time. However, it can be observed in both the tensile strength and elongation at break that the film without benzophenone had the greatest decrease in tensile properties compared to the others. These results were different from the photodegradation test in which the



(a)



(b)

Figure 18 The (a) tensile strength and (b) elongation at break of LDPE/10% banana starch/10% PE-g-MA film containing different amounts of benzophenone during the soil burial test.

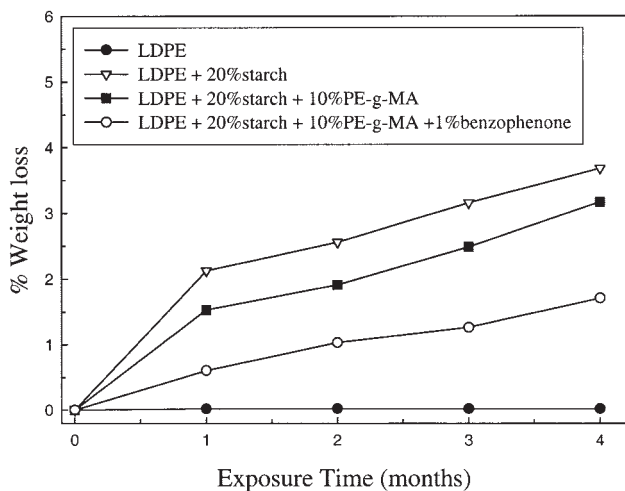


Figure 17 The weight loss of pure LDPE, LDPE/20% banana starch, LDPE/20% banana starch/10% PE-g-MA, and LDPE/20% banana starch/10% PE-g-MA/1% benzophenone films.

increase in benzophenone content helped promote the decrease in tensile properties of the blend films being subjected to the outdoor exposure test. However, these results were similar to the weight loss measurement in which the increase of the benzophenone concentration decreased the biodegradability of the films.

In addition, these results are in good agreement with the SEM micrographs shown in Figure 15. The LDPE/starch films containing 1% benzophenone showed a small amount of holes on the film surface. This is because the benzophenone in the blend films inhibits the growth of microorganisms, resulting in the reduction of starch consumption by microorganisms. Therefore, the films containing higher content of benzophenone had small decreases in tensile strength and elongation at break as a function of time. After 4

months, the tensile strength and elongation at break of the blend film with 1% benzophenone decreased about 1.9 and 17.6%, respectively, whereas the tensile strength and elongation at break of the film without benzophenone decreased approximately 11.5 and 28.2%, respectively. Based on these results, it can then be concluded that benzophenone has a small inhibiting effect on the biodegradation rate of these systems.

CONCLUSION

Banana starch and benzophenone were found to be effective additives in LDPE films because they promoted the degradation of this polymer. The presence of both additives in the films led to a material that degraded faster than pure LDPE.

As the banana starch content increased, the carbonyl index of the films after photodegradation by an outdoor exposure test increased whereas the tensile strength decreased. Banana starch that was intended to function as a biodegradation additive also enhanced the photodegradation of the films by increasing the number of holes in the LDPE matrix. With increasing banana starch content, there were more gaps between the LDPE and starch granules that allowed the permeation of light and oxygen into the inner part of the LDPE, causing photodegradation of the films. In addition, after biodegradation by a soil burial test, the LDPE film was not degraded but the LDPE films containing various amounts of banana starch were obviously degraded as a function of the starch content. Similarly, as the starch content increased, there were more sites on the film surface that could be attacked by microorganisms. The presence of the tiny holes observed in the SEM micrographs of LDPE/starch films confirmed that the banana starch was removed from the LDPE matrix after biodegradation, resulting in the increase in weight loss and the reduction in tensile properties of the films.

Although the addition of PE-g-MA in the LDPE/banana starch films led to an increase in tensile strength, it was found that the biodegradability of the film containing PE-g-MA as a compatibilizer was slightly less than the films without PE-g-MA. This implied that the compatibilizer had an inhibiting effect on the degradation of the films. The effect of PE-g-MA may be due to the bonding between anhydride groups of PE-g-MA and hydroxyl groups of starch, which obstructs the consumption of starch from microorganisms.

Benzophenone functioned as a good photosensitizer for the LDPE/starch films. The photodegradation of LDPE/starch films increased with increasing benzophenone content as determined by an increase in the carbonyl index, as well as a decrease in the tensile strength of the films after the photodegradation test. However, the results revealed that benzophenone had

a small inhibiting effect on the biodegradation rate of LDPE/starch films.

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