

# Studies on the Degradable Polyethylenes: Use of Coated Photodegradants with Biopolymers

BYUNG SEON YOON,<sup>1</sup> MOON HO SUH,<sup>1</sup> SHI HWA CHEONG,<sup>2</sup> JAE EUE YIE,<sup>2</sup> SUNG HWA YOON,<sup>2</sup>  
and SUCK HYUN LEE<sup>2,\*</sup>

<sup>1</sup>Department of Chemical Engineering and <sup>2</sup>Department of Applied Chemistry, Ajou University,  
Suwon 442-749, South Korea

## SYNOPSIS

Three degradable polymer materials such as starch–polyethylene (PE) binary blends, PE containing starch and a photoactivator, and PE containing starch and a photoactivator which was coated with gelatin were prepared and their degrees of photodegradation and/or photodegradation after biodegradation were investigated. The addition of the gelatin-coated ferric salt in PE extended the induction period of degradation and accelerated photodegradation after the removal of coating material by biodegradation. This result suggested that the degradation rate of PE could be controlled if more powerful photoactivators and/or coating material are developed and their contents are optimized. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The environmental pollution of waste plastic has been recently recognized to be a serious problem. To overcome the problems, natural polymers derived from animal and/or plants, biosynthetic polymers from microorganisms, and some synthetic polymers were extensively studied.<sup>1–4</sup> While natural polymers and some synthetic polymers are readily decomposed in the environment during their lifetimes, most synthetic polymers have a resistance to degradation by microorganisms in spite of their good physicochemical properties such as transparency and flexibility and their mechanical properties. Therefore, various studies were carried out to achieve the promotion of the degradation of synthetic polymers such as polyethylene (PE) by addition of biodegradants and/or photodegradants fillers.<sup>5</sup>

Among these studies, the Ecolyte process<sup>2,6</sup> developed by Guillet et al. at Toronto University, Canada, promotes Norrish-type photodegradation by introducing a carbonyl group into PE. The Eco-star system<sup>6–8</sup> developed by Griffin et al. increases

the decomposition rate by addition of starch as well as an autooxidant into PE. Although the mechanism of autooxidants, which are mostly composed of the unsaturated fatty acid and transition metals, is not fully understood,<sup>9</sup> it is recognized that it takes a long time to reduce the molecular weight of PE.

The Scott–Gilead process,<sup>5,10,11</sup> which is now commercially used in degradable polymers, is based on the addition of certain metalloorganic complexes which act as chromophores and a light-controlled catalyst. Many transition metals such as nickel and cobalt have been used as photoantioxidant additives; iron and the manganese complex were revealed to be much less stable and to undergo photolysis after the induction period.<sup>10,11</sup> The success of the above antioxidant–photoactivator system relies on the time control offered and ultimate biodegradation of photooxidized products. Their potential limitations are in food-contact applications due to the toxicity of the additives.

Most of degradation process of PE proceeds with two interactive mechanisms with additives or photoactivators. These mechanisms are based on either biodegradation by microorganisms or photolysis by additives such as an autooxidant and photoactivator. Of the new additives for the degradation process with PE, we studied photoactivators coated with biode-

\* To whom correspondence should be addressed.

**Table I Physical Properties of the HDPE Neat Resin**

$M_w$	Density	$T_m$ (°C)	Tensile Strength	Flexural Strength	Elongation
$2.04 \times 10^5$	0.95	128.3	22.5 (MPa)	870 (MPa)	730%

gradable polymers as new additives for the sequenced bio- and photodegradation of polymers. This approach could be advantageous over previous methods because (1) the degradation rate might be controlled by varying the coated thickness of the photoactivator and the contents of the additives and (2) the coloring of composite films and the toxicity of the additives could be alleviated by the coating process.

In our preliminary studies to probe our approach, we focused on measuring the yield stress as well as the strain at break of the samples, which contain different additives, to evaluate whether samples sustain the lifetime of mechanical properties on exposure time. In the present article, we report the preparative methods of additives and the physical properties of PE film filled with prepared additives.

## EXPERIMENTAL

### Methods of Biodegradation and Photodegradation

#### Materials

The basic HDPE (TR 144), donated by the Daelim Co., Daejeon, South Korea, has a weight-average molecular weight ( $M_w$ ) of  $2.04 \times 10^5$ , a density of 0.95, and a melting temperature 128.3°C, and its physical properties are described in Table I. Corn starch purchased from the Sigma Chemical Co. as extrapure grade was dried under a vacuum (20 mmHg) at 100°C to a final moisture content of less

than 0.5%. The content of starch in HDPE was varied in the range of 0–15 wt %, and the concentration of the photoactivator in PE was 0.6 wt %. Their blend compositions are described in Table II. Mixing was performed by using a roll-type mixer of Haake Rheomix for 15 min at 180°C with a roll speed of 30 rpm and then the prepared materials were transferred to a desiccator immediately. The films (150 × 150 mm with a thickness of 200–250 μm) were prepared by compression molding at 150°C and 500 kPa.

#### Biodegradation

The α-amylase purchased from Sigma was used for the measurement of biodegradation of starch–HDPE film in acetate buffer, pH 6, while the protease enzyme purchased from Sigma was used for the photodegradation of the films in acetate buffer, pH 7.8. A small amount of sodium azide was added to the testing solution for inhibition of the growth of fungi. All samples were incubated for 14 days at 37°C before testing.

#### Photodegradation

Films were exposed to a UV chamber equipped with 6 lamps (312 nm, 15 W) at 50°C in an aluminum chamber of 80 × 65 × 60 cm.

#### Manufacture of the Coated Photoactivator

The photoactivator was coated with gelatin by the coacervation method.<sup>12,13</sup> The gelatin (Shinyo A) and

**Table II Blend Compositions**

Mixture HDPE/Additive	HDPE (Wt %)	Starch (Wt %)	Ferric Dithiodicarbamate (Wt %)
100/0	100	0	0
95/5	95	5	0
90/10	90	10	0
85/15	85	15	0
99.4/0.6	99.4	0	0.6
99.4/0.6	99.4	0	0.6 <sup>a</sup>

<sup>a</sup> The ferric dithiodicarbamate was coated with gelatin by the coacervation method.

sodium sulfite were purchased from the Shinyo Co., Japan, and glutaraldehyde was purchased from the Fluka Co. as a reagent grade.

The procedure of coating is as follows: The gelatin solution (100 mL, 2% w/v) was added to 80 mL of a ferric salt solution in ethanol (95% w/v) and stirred at 35°C. The glutaraldehyde solution (25% w/v, 50 mL) was then added to the resulting ferric salt for cure. After addition of the sodium sulfite solution (100 mL, 12% w/v) to remove the unreacted glutaraldehyde, the remaining emulsion was stirred for 15 min, then cooled followed by filtration through a polycarbonate membrane (3  $\mu\text{m}$  pore size) to give the desired coated photoactivator, which was finally dried under a vacuum condition.

## Measurement of Degradation

### *Infrared Spectroscopy Method*

The degradabilities of the polymer blends were evaluated by measuring the changes of the absorption coefficients of carbonyl (1718  $\text{cm}^{-1}$ ), vinyl (908  $\text{cm}^{-1}$ ), and hydroxyl (3400  $\text{cm}^{-1}$ ) peaks before and after degradation of the polymer films of 10–15  $\mu\text{m}$  thickness.

### *Mechanical Properties*

Yield stress and strain at break of the samples (200–250  $\mu\text{m}$  thickness) were tested according to the ASTM D882-83 method with UTM (Instron Co.). The testing speed was set at 500 mm/min with 50% relative humidity.

### *Morphological Methods*

Scanning electron microscopy analysis was performed with an Akashi ISI-DS-130 and the surface of the films which were coated with gold was observed.

### *Weight Determination*

The amount of decreasing weight was calculated as a percent of the initial sample weight. The tested samples (30  $\times$  30 mm) were prepared and conditioned in a desiccator for 2 days before the initial weight was measured.

## RESULTS AND DISCUSSION

### *PE/Starch Blends*

Commercially available starches from corn, wheat, potato, and rice are composed of spherulite particles

whose diameter varies in the range of 2–150  $\mu\text{m}$ . These crystalline structures are destroyed with the elevation of temperature (65–80°C) by absorbing water and then are gelatinized. The moisture in starch can act as a reactive plasticizer or lubricant at high temperatures.

From the preliminary experiments of extrusion blending, we found that bubbles were formed inside the film even at a 0.5% level of water content. Therefore, in this study, we kept a high extrusion temperature and a low screw speed to reduce the water content by the eventual gelatinization reaction.

As shown in Figure 1, the SEM photography of the manufactured 15% starch-contained film showed less than 20  $\mu\text{m}$  for the size of the starch and pretty good dispersion was obtained. It was also observed that the area surrounding the starch particles in the film biodegraded by  $\alpha$ -amylase turned white, indicating that the density of the particle surface decreased during the process of biodegradation.

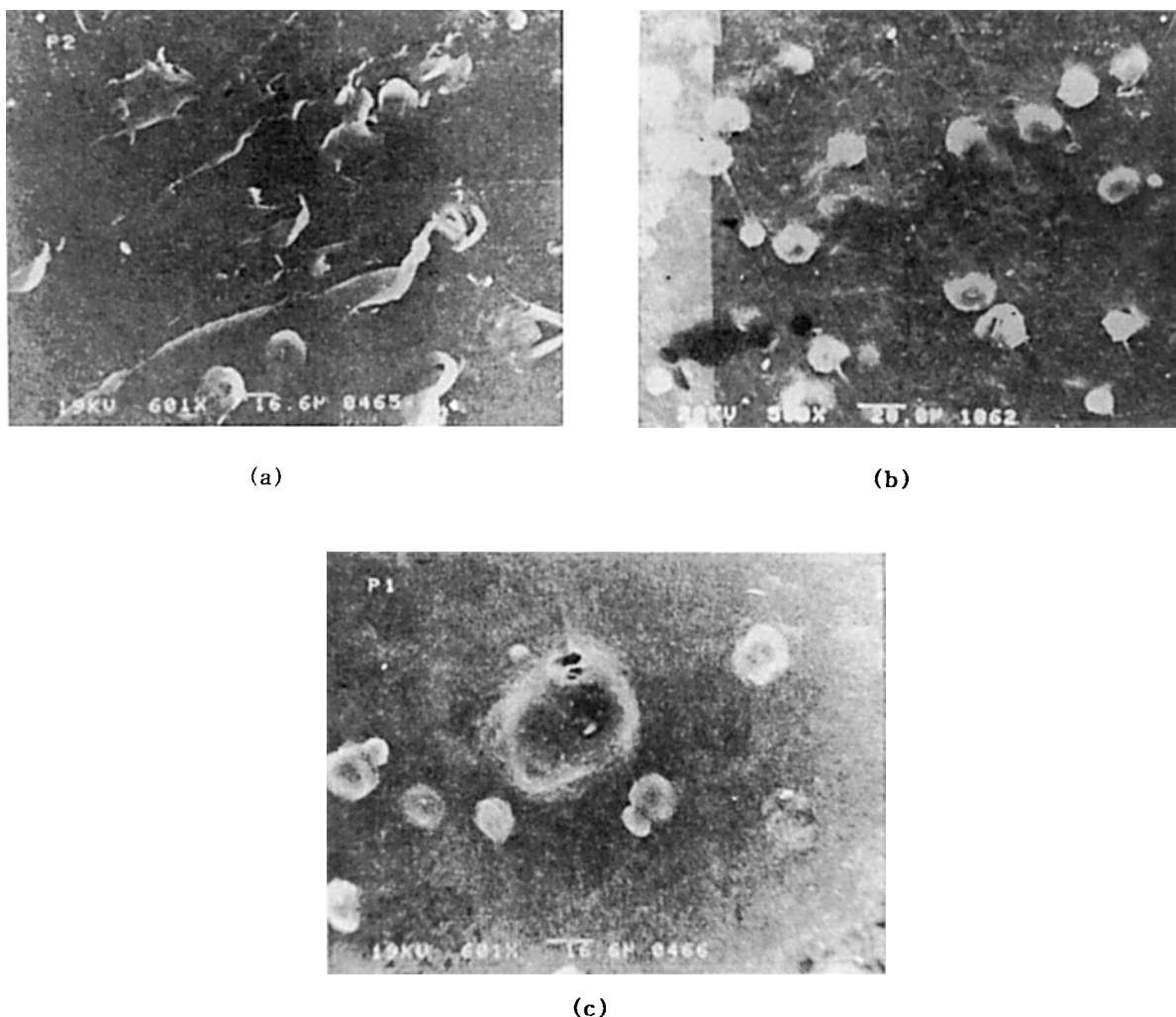
Figure 2 shows the weight loss of HDPE/starch films against biodegradation time in the  $\alpha$ -amylase solution. The weight decreased significantly at the beginning of the degradation process, possibly due to the biodegradation of starch at the surface of the tested films. After the first 2 days, the weight decreased gradually and the weight loss was linear with biodegradation duration.

Figure 3 shows the relationship between yield stress and biodegradation time. Generally, yield stress did not change much during the 14 days of biodegradation. The case of the 15% starch content showed the largest change, in which the yield stress decreased only about 25% of the initial value. However, the strain at break was changed dramatically and was more sensitive to the biodegradation period (Fig. 4).

### *The PE Containing Bio/photoactivator*

#### *Coated Photooxidant*

The combination of biodegradation and photodegradation relies on either the way which a product of photodegradation promotes biodegradation and vice versa or the way which bio/photodegradation occurs simultaneously. Until recently, most of combination studies of bio- and photodegradation were focused on the development of the process, in which the oxidation products by photodegradation were treated by biodegradation thereafter. However, these methods resulted in a long degradation time to reach to the biodegradable molecular weight of the base



**Figure 1** SEM of HDPE films containing 15% starch in  $\alpha$ -amylase solution: (a) 0 day, (b) 2 days; (c) 4 days.

polymer and this long degradation time leads to other environmental pollution due to partially deteriorated segments of PE.

To overcome these problems, the new protection-destruction mechanism was tried in this study to manufacture the photooxidative additives coated with biopolymer. Since this system could provide stabilization, the initial mechanical strength of the films is maintained until the complete biodegradation of the coated layer.

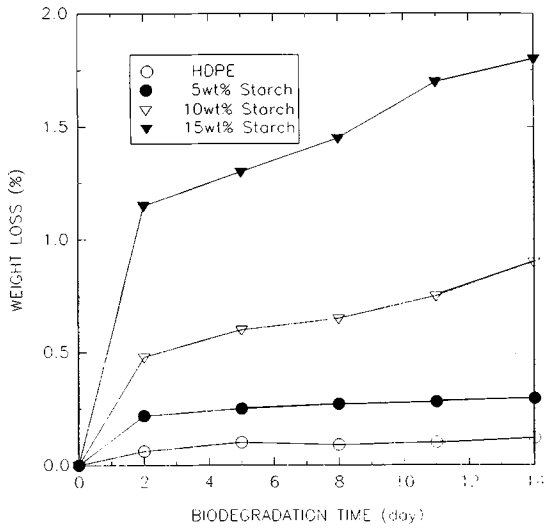
Figure 5 shows the shape of the particle coated with gelatin by coacervation. We tried to manufacture the Fe(III) dithiodicarbamate used as the photoactivator as a fine powder by ball milling, but the particle shape and its size were not uniform. As regards the results, the coated particles were not spherical shaped and their sizes varied in the range of 0.5–2.5  $\mu\text{m}$ .

To confirm the coating of photoactivator particles, the UV absorbability and the release rate of the interior material were measured after the coated material was dispersed in a solvent which did not dissolve the coated gelatin.

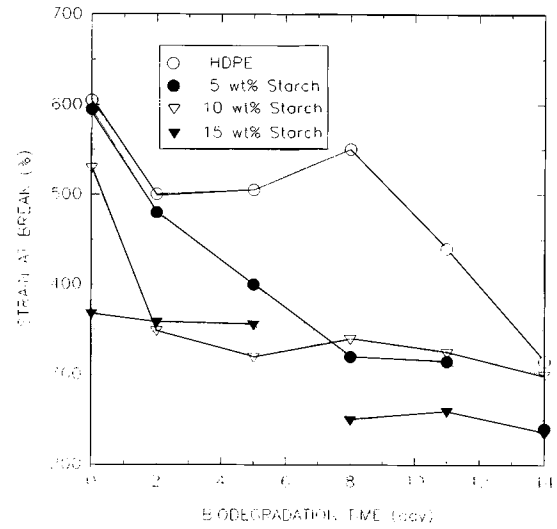
Figure 6 shows the relationship between UV absorptivity and the material releasing time. It could be confirmed that the inner material diffuses through the film from the linear relationship of UV absorption against  $t^{1/2}$ . The coated fraction of particles was calculated from this relationship since the absorptivity at  $t = 0$  is related to the uncoated or partially coated particles. In this way, we found that the degree of coating was about 60%.

#### **Mechanical Properties**

After manufacturing based PE and the PE containing 0.6 wt % ferric salt coated with gelatin, we com-

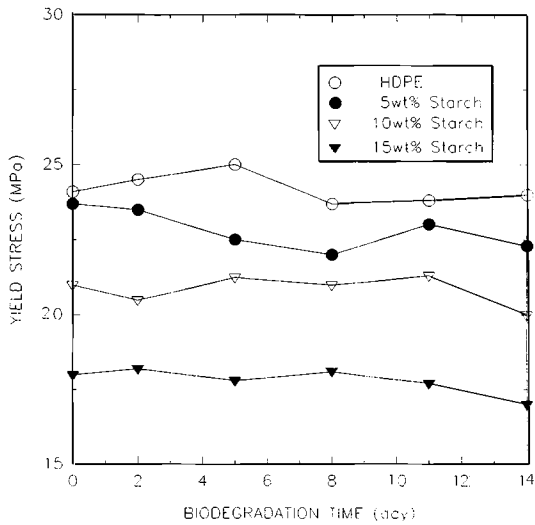


**Figure 2** Weight loss of HDPE/starch films vs. biodegradation time in  $\alpha$ -amylase solution: (a) (O) HDPE; (b) (●) 5 wt % starch; (c) (▽) 10 wt % starch; (d) (▼) 15 wt % starch.

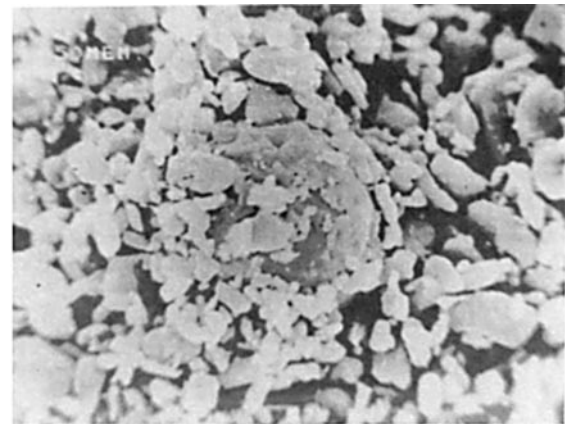


**Figure 4** Change of strain at break vs. biodegradation time in  $\alpha$ -amylase solution: (a) (O) HDPE; (b) (●) 5 wt % starch; (c) (▽) 10 wt % starch; (d) (▼) 15 wt % starch.

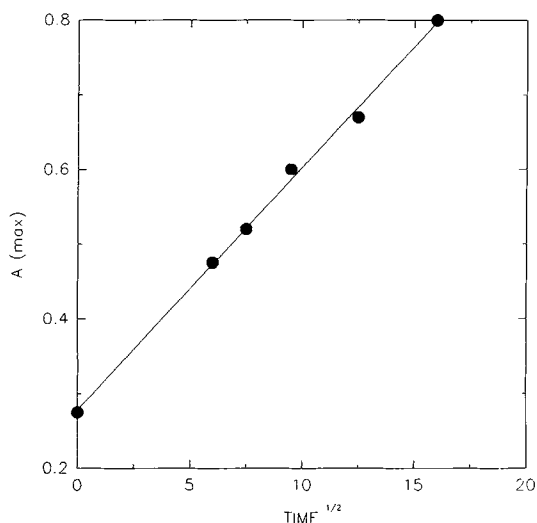
pared the mechanical properties of both samples according to photodegradation times. Figures 7 and 8 show the change of yield stress and strain at break of the based PE film (PPE), simple PE film loaded with ferric salt (PFA), and PE film loaded with gelatin-coated ferric salt (PCA) as a function of the photolysis time. In comparison with based PE, the PE film containing ferric salt showed a repeated increment/decrement of yield stress from the beginning, while the PE film containing ferric salt coated



**Figure 3** Change of yield stress vs. biodegradation time in  $\alpha$ -amylase solution: (a) (O) HDPE; (b) (●) 5 wt % starch; (c) (▽) 10 wt % starch; (d) (▼) 15 wt % starch.

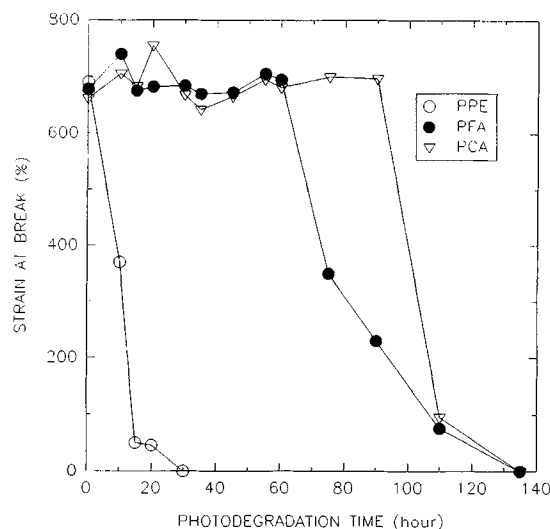


**Figure 5** SEM of the ferric salt-loaded gelatin microcapsules by coacervation (magnification: 4.05K).



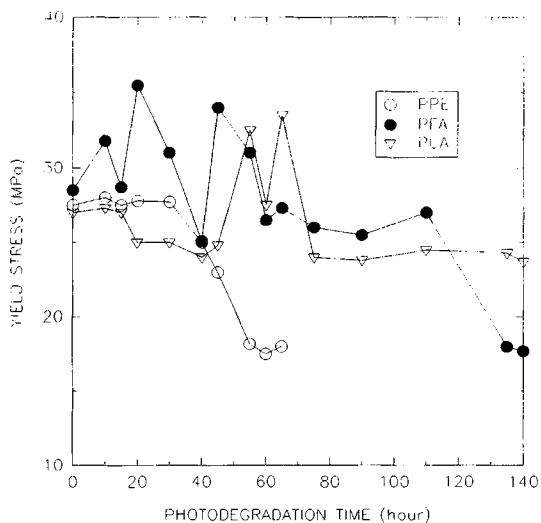
**Figure 6** Change of A(max) vs. the material releasing time using UV spectrum.

with gelatin sustained the strain at break during 50 h followed by a repeated increment/decrement between 50 h and 80 h and then sustained the stability until 140 h. In particular, in the case of the PE film containing ferric salt coated with gelatin, the induction period extended about 30 h and the decrement rate in the strain at break was steeper, as we expected. It is of interest to note that the mechanical property of the PE film containing ferric salt coated with gelatin showed the repeated increment/decrement phenomena instead of reduction at the beginning of photolysis. This could be explained by

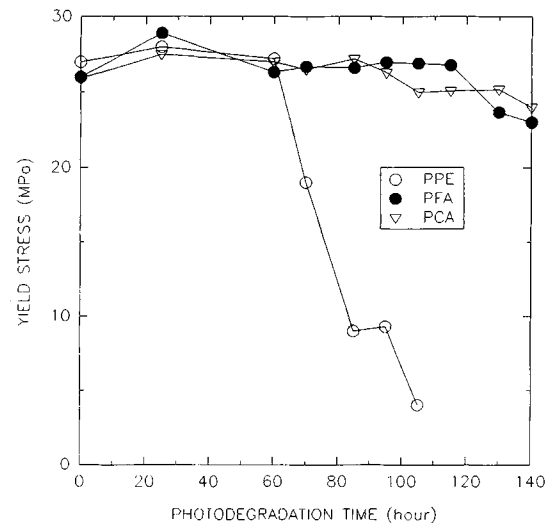


**Figure 8** Change of strain at break vs. photodegradation time in UV chamber: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.

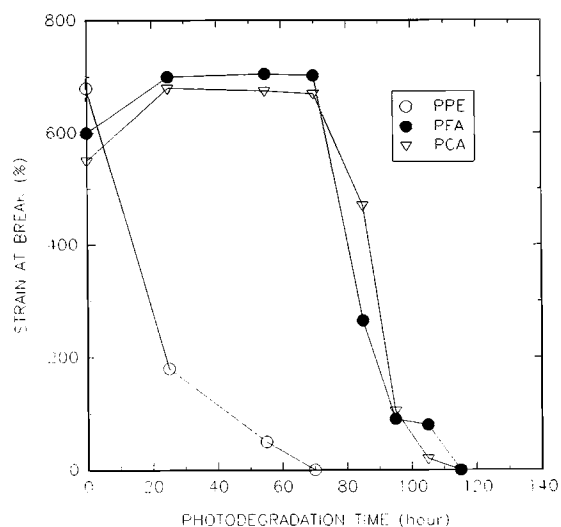
that the increment of the mechanical property is due to UV-initiated crosslinking between PE chains, while the decrement is due to the scission of the main chain.<sup>14,15</sup> Figures 9 and 10 show the mechanical properties of based PE film (PPE), the PFA, and the PCA PE film against the decomposition time by photolysis after biodegradation for 5 days. In comparison with photolysis without biodegradation, the PE film containing ferric salt did not show any changes in yield stress for 140 h, while its strain at break decreased sharply after 80 h. However, there was not much difference in the mechanical prop-



**Figure 7** Change of yield stress vs. photodegradation time in UV chamber: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.



**Figure 9** Change of yield stress vs. photodegradation time in UV chamber after 5 days in protease solution: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.



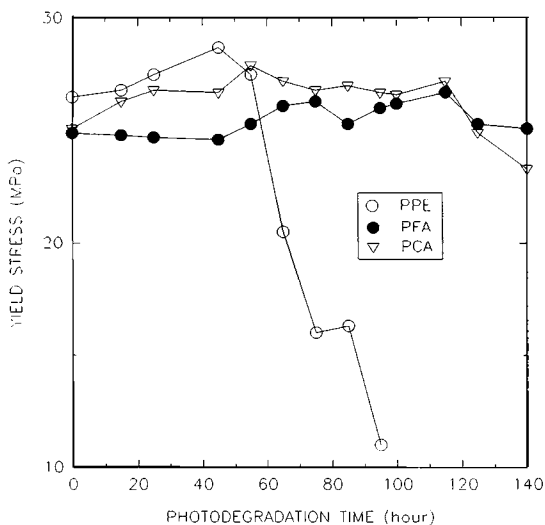
**Figure 10** Change of strain at break vs. photodegradation time in UV chamber after 5 days in protease solution: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.

erties between coated ferric salt and uncoated ferric salt.

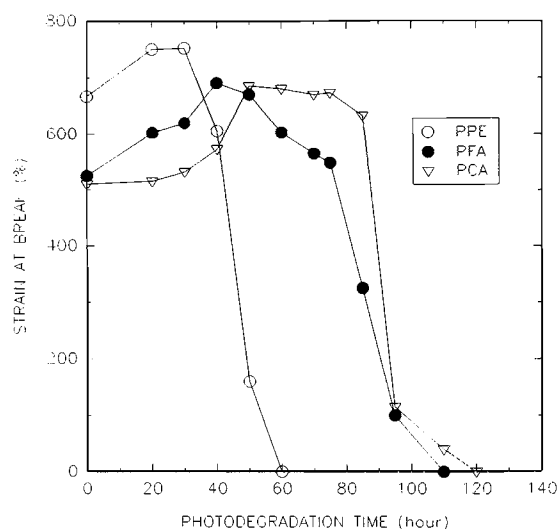
Similar trends were also observed in 10 days' biodegradation for the tested films (Figs. 11 and 12). These results indicated that the gelatin layer of coated particles was completely decomposed by the enzyme during the initial 5 days.

#### The Chemical Changes of the PE Films According to Photodegradation Time

The degree of chemical degradation was calculated from the absorption changes of the functional group



**Figure 11** Change of yield stress vs. photodegradation time in UV chamber after 10 days in protease solution: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.

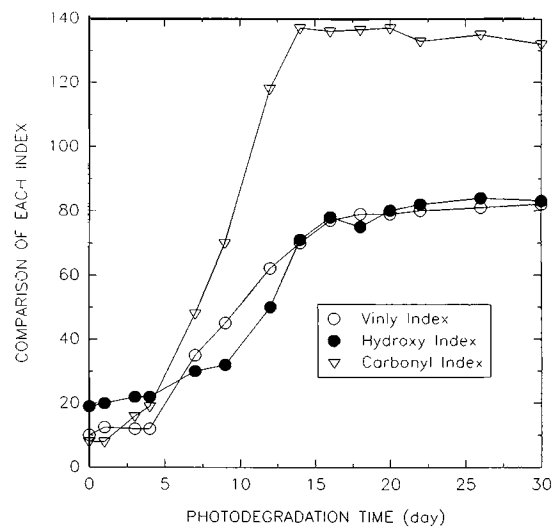


**Figure 12** Change of strain at break vs. photodegradation time in UV chamber after 10 days in protease solution: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.

such as carbonyl, vinyl, and hydroxyl measured by IR. Since the intensities of the absorbed light are dependent on the film thickness and instrument condition,<sup>16</sup> we used here the relative spectral index as defined in the following:

$$\text{Spectral index} = \frac{\text{absorbance of functional group}}{\text{absorbance at } 1890 \text{ cm}^{-1}}$$

The defined index can reduce the error from the thickness of samples because absorbance is propor-



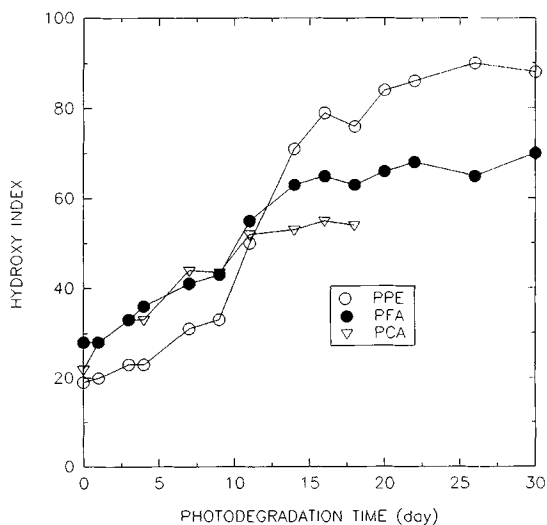
**Figure 13** Change of functional group indices vs. photodegradation time in UV chamber for PPE film: (a) (○) vinyl index; (b) (●) hydroxy index; (c) (▽) carbonyl index.

tioned to the PE film thickness. Therefore, in case of the PEs, we selected the absorbance at  $1890\text{ cm}^{-1}$  as the internal standard and calculated the relative absorbance of the carbonyl index ( $1710\text{ cm}^{-1}/1890\text{ cm}^{-1}$ ), vinyl index ( $908\text{ cm}^{-1}/1890\text{ cm}^{-1}$ ), and hydroxyl index ( $3400\text{ cm}^{-1}/1890\text{ cm}^{-1}$ ).

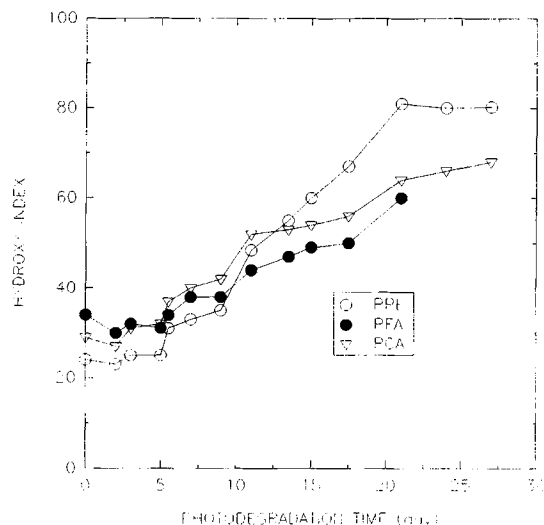
Figure 13 shows three indices of a based PE according to the time. Although all indices were increased steeply for the first 14 days and increased gradually later, the absorbance of the carbonyl index was higher than that of the other indices.

Figures 14 and 15 show the change of the hydroxyl index according to the photodegradation time after the proceeding of biodegradation for 5 days. Although there was not much difference in the hydroxyl index between the film containing coated ferric salt and the film containing the uncoated one at the beginning of photodegradation, the hydroxyl indices of both films were higher than that of the based PE. However, these phenomena were reversed after 14 days and were also observed in the other two indices.

As shown in Figure 15, the hydroxyl index against photodegradation time after 5 days' proceeding of biodegradation showed a different tendency. The hydroxyl index of the film containing the coated ferric salt was higher than that of the film containing the uncoated ferric salt. Since the hydroxyl group in the PE is closely related to the chain scission by the radical, the increment of the hydroxyl index means a larger chemical change. These results indicate that the stabilization effect of the photoac-



**Figure 14** Change of hydroxyl index vs. photodegradation time in UV chamber: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.



**Figure 15** Change of hydroxyl index vs. photodegradation time in UV chamber after 5 days in protease solution: (a) (○) PPE; (b) (●) PFA; (c) (▽) PCA.

tivator was obtained by coating with gelatin and that the coated photoactivator was rather promoted after biodegradation in comparison with the uncoated one.

## CONCLUSION

In this study, new additives were applied into PE to accelerate photodegradation after biodegradation. Ferric dithiocarbamate and gelatin were selected as for the additive and coating material, respectively. When the content of additive in PE was maintained at 0.6 wt %, the longer induction period as well as the acceleration of photodegradation after the removal of the coating material by biodegradation were observed in the films containing additives. This result suggested that the important properties of the polymer could be maintained by addition of coated materials which can be varied in type and/or concentration as to give reliably reproducible life spans of a polymer.

We are grateful to the Daelim Co. for financial support.

## REFERENCES

1. T. M. Aminabhavi and R. H. Balundgi, *Polym. Plast. Technol. Eng.*, **29** (3), 235 (1990).



2. J. E. Guillet, in *Degradable Materials*, S. A. Barenberg, J. L. Brash, R. Narayan, and A. E. Redpath, Eds., CRC Press, Boston, 1990, p. 55.
3. G. Swift, in *Agricultural and Synthetic Polymers Biodegradability and Utilization*, J. E. Glass and G. Swift, Eds., American Chemical Society Press, Washington, DC, 1990, Chap. 1.
4. F. H. Otey, A. M. Mark, C. C. Mehlter, and C. R. Ressel, *Ind. Eng. Chem. Prod. Res. Dev.*, **13**, 19 (1974).
5. G. Swift, in *Degradable Materials*, S. A. Barenberg, J. L. Brash Ramani Narayan, and A. E. Redpath, Eds., CRC Press, Boston, 1990, p. 143.
6. W. J. Maddever and G. M. Chapman, *Plast. Eng.*, **July**, 31 (1989).
7. G. J. L. Griffine, U.S. Pat. 4,016,117 (1977).
8. G. J. L. Griffine, U.S. Pat. 4,021,288 (1977).
9. P. P. Klenehk, *Mod. Plast.*, **19**, 82 (1989).
10. D. C. Meller, A. B. Moir, and G. Scott, *Eur. Polym. J.*, **9**, 219 (1973).
11. G. Scott, H. H. Sheua, and A. M. Harriman, *Eur. Polym. J.*, **14**, 1071 (1978).
12. R. C. Oppenheim et al., U.S. Pat. 4,107,288 (1978).
13. P. B. Deasy, *Microencapsul. and Rel. Drug Processes, (Drugs and Pharm. Sci.)*, 20 (1984).
14. A. C. Alberton and S. Karlsson, *J. Appl. Polym.*, **35**, 1289 (1988).
15. J. F. Rabek, Eds., in *Stabilization of Polymer*, Elsevier, New York, 1990, Chap. 1.
16. D. C. Mellor, A. B. Moir, and G. Scott, *Eur. Polym.*, **9**, 219 (1973).

Received August 29, 1995

Accepted December 11, 1995