

Soil Burial Test for Poly(ethylene-*co*-vinyl alcohol)-graft-Polycaprolactone

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ABSTRACT: The ring-opening polymerization of ϵ -caprolactone was carried out with poly(ethylene-*co*-vinyl alcohol) as a macroinitiator to synthesize poly(ethylene-*co*-vinyl alcohol)-graft-polycaprolactone (EVOH-*g*-PCL). A simple low-density polyethylene (LDPE)/polycaprolactone (PCL) (64/36) blend lost 5.3 wt % of its original weight after 90 days of a soil burial test. However, the elongation at break of the LDPE/PCL blend remained almost invariable even after the solid burial test because the tensile properties depended mostly on the LDPE phase on account of the poor interaction between the continuous LDPE matrix and the dispersed PCL phase. For EVOH-*g*-PCL, the elongation at break decreased drastically as a result of the soil burial test, and the reduction of the elongation at break was more pronounced for EVOH-*g*-PCL with a higher PCL concentration, even though the

weight loss of EVOH-*g*-PCL after the soil burial test was as low as 1.2–1.3% and was nearly independent of the PCL concentration. Few holes were observed in EVOH-*g*-PCL when the PCL concentration was less than 26 wt % after an accelerated hydrolysis experiment at 60°C for 7 days in a 0.1M KOH solution. In contrast, the hydrolysis formed small holes in EVOH-*g*-PCL with a PCL concentration of 36 wt %. The LDPE/PCL blend was much better percolated, as a result of the hydrolysis, than EVOH-*g*-PCL with the same PCL concentration; the soil burial test showed the same results. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1064–1071, 2005

Key words: biodegradable; blends; degradation; graft copolymers

INTRODUCTION

Biodegradable polymers are used in numerous applications, such as surgical implants,¹ sutures,² and controlled-release drugs.^{3–7} Research has been conducted to develop low-cost biodegradable polymers to reduce the solid waste produced by many artificially synthesized polymers. Hardly degradable plastics used for single-use receptacles, fishing tools, and the packaging of fresh meat and fish could be targets for replacement with biodegradable materials.

Biodegradable polymers also are useful for agriculture in mulch,^{8–10} controlled-release fertilizers,¹¹ and pesticides.⁸

Refuse-collection plastic bags also require degradation to stabilize the foundation of soil burial sites and to prevent water-clogging phenomena; for this, the biodegradable fraction in compounds made of biodegradable components and a hardly degradable matrix should be greater than the percolation level.

In this study, polycaprolactone (PCL) was grafted to poly(ethylene-*co*-vinyl alcohol) (EVOH) through the

ring-opening polymerization of ϵ -caprolactone (CL) with EVOH as a macroinitiator.

The PCL content in the graft copolymer [poly(ethylene-*co*-vinyl alcohol)-graft-polycaprolactone (EVOH-*g*-PCL)] was raised up to 36 wt %, which was greater than the percolation level. The degradation of the graft copolymer was carried out in an activated sludge soil for 90 days. The weight reduction and the variation of the tensile properties of the graft copolymer were followed with respect to the degradation time and were compared with those of a simple linear low-density polyethylene (LDPE)/PCL blend. LDPE was chosen from the different kinds of polyethylenes because poly(ethylene-*co*-19 wt % vinyl acetate) (EVA19), the mother polymer for EVOH synthesis, is usually produced commercially in a high-pressure reactor, like LDPE.

EXPERIMENTAL

Materials (Table I)

CL (Aldrich, Milwaukee, WI) and stannous 2-ethyl hexanoate (Aldrich) were used as received. LDPE [melt index = 5, weight-average molecular weight (M_w) = 482,000] and EVA19 (M_w = 75,000) were donated by Hanhwa (Ulsan, Korea). Other chemical compounds were reagent-grade and were used as received.

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TABLE I
Characteristics of the Polymer Materials

Sample code	T_m (°C)	T_c^a (°C)	ΔH_f^b (J/g of EVOH)	M_w ($\times 10^{-3}$)
PCL	62.4	23.3	83.5	117
LDPE	106.2	85.0	66.3	482
EVA19	81.2	56.2	70.8	75
EVOH19	102.6	80.3	51.8	61

^a T_c : crystallization temperature.

^b ΔH_f : heat of fusion.

Instrumentation

The molecular weight and molecular weight distribution were measured with gel permeation chromatography (GPC; model 150C, Waters, Milford, MA) with 1,2,4 trichlorobenzene as the eluent (1.0 mL/min at 135°C), Styragel columns [10- μ m porosity; HT6E (effective molecular weight range = 5100– 1×10^7), HT5 (effective molecular weight range = 5100– 4×10^6 , and HT3 (effective molecular weight range = 500–30,000)], and polystyrene (SL-105, Showa Denko, Kanagawa, Japan) as a standard. The graft copolymer was characterized with ¹H-NMR spectra recorded at 110°C on a Bruker AC-250 FT-NMR spectrometer (Rheinstetten, Germany). The copolymer (10 mg) was dissolved in 0.5 mL of 1,2-dichlorobenzene-*d*₄ (20 w/v) and was subjected to ¹H-NMR measurements.

The thermal properties of the polymers were determined with differential scanning calorimetry (DSC; DSC 7, PerkinElmer, Boston, MA). The thermal history of the polymers was removed via scanning to 200°C at a heating rate of 20°C/min (first scan). After the samples cooled at a rate of -5°C/min to room temperature, they were reheated at 20°C/min to 200°C, and second DSC scan thermograms were obtained.

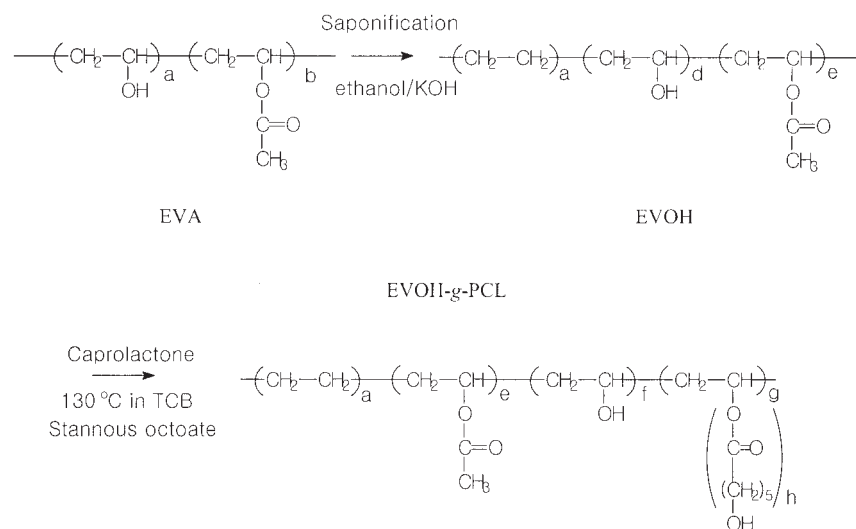
Soil burial test specimens (0.25 ± 0.05 mm thick) were made via hot pressing at 200°C for 5 min under 1.55 atm and were quickly immersed in ice water. The films thus formed were free of any distortion problems.

The mechanical properties were determined with a tensile test machine (model 4200, Instron, Grove, PA) at a crosshead speed of 50 mm/min according to ASTM D 638 at 20°C and at a relative humidity of 65 ± 1%.

Each sheet was fractured while immersed in liquid nitrogen. Scanning electron microscopy (SEM; S-4200, Hitachi, Tokyo, Japan) was used to observe the fractured surface morphology.

Preparation of EVOH¹²

Poly(ethylene-*co*-vinyl acetate) (EVA) pellets were ground into a powder (ca. 250 μ m). Ground EVA (6 g) was saponified in 200 mL of 0.5M KOH in an ethanol solution (1000 mL of ethanol/28.05 g of KOH):



The saponified EVA was not soluble in the reaction system. The heterogeneous solution was refluxed with stirring for 15 min to 72 h, precipitated with excess distilled water, filtered, washed with distilled water and methanol, and dried *in vacuo*. The concentrations of the copolymers were determined from ¹H-NMR peaks of methine protons (4.9 ppm) and methyl protons (2.1 ppm) of vinyl acetate units with eqs. (1) and (2):

$$\frac{3b}{4a + 6b} = \frac{\text{Peak at 4.9 ppm and 2.1 ppm}}{\text{Total peak area}} \quad (1)$$

$$\frac{3e}{4a + 3d + 6e} = \frac{\text{Peak at 4.9 ppm and 2.1 ppm}}{\text{Total peak area}} \quad (2)$$

$$\text{Degree of saponification} = \frac{b - e}{b} \times 100 (\%) \quad (3)$$

TABLE II
Synthesis of the EVOH-g-PCL copolymer

Sample code	Polymerization time (h)	Copolymer yield (g)	PCL (wt %)	PCL homopolymer (g)	T_m of EVOH (°C)	ΔH_f^b (J/g of EVOH)	T_c^c of EVOH (°C)	M_w ($\times 10^{-3}$) ^a
EVOH	—	6.00	—	—	102.6	51.8	80.3	61
EVOH-g-PCL16	24	7.11	15.6	0.2	96.6	42.4	77.2	89
EVOH-g-PCL26	48	8.07	25.7	0.5	95.0	34.3	74.5	104
EVOH-g-PCL36	72	9.35	35.8	0.4	94.5	31.3	74.2	236

Polymerization temperature = 130°C.

^a Measured from GPC.

^b ΔH_f^b : heat of fusion. ^c T_c^c : crystallization temperature.

Synthesis of EVOH-g-PCL (Table II)

The saponified EVOH (6 g) was dissolved in 1,2,4-trichlorobenzene (50 mL), and then CL (5 mL) and stannous 2-ethyl hexanoate (0.2 mL) were added. The polymerization was carried out at 130°C for 24–72 h. The product was precipitated into methanol and dried *in vacuo*; this was followed by Soxhlet extraction with boiling ethanol for 1 day to remove the PCL homopolymer byproduct that formed during the graft copolymerization.

Polymer blending

An LDPE/PCL mixture was first dissolved in 1,2,4-trichlorobenzene at 140°C and kept under an N₂ blanket to prevent oxidation. After 30 min of stirring, the

product was precipitated in methanol and dried *in vacuo* at 60°C.

Determination of biodegradability by soil burial testing

Specimens in the form of rectangular sheets were buried in activated sludge soil collected from the Nanjido Municipal Wastewater Treatment Plant in Seoul, Korea (the composition of the activated sludge soil was 35.7% carbon, 5.27% hydrogen, 4.23% nitrogen, and 1.23% sulfur). The activated sludge soil was loaded into a foamed polystyrene box (220 mm \times 220 mm \times 150 mm). At predetermined intervals, polymer specimens were removed from the soil, cleansed with water, and dried in a vacuum oven. The dried specimens were weighed to calculate the weight loss. Five measurements were taken on average.

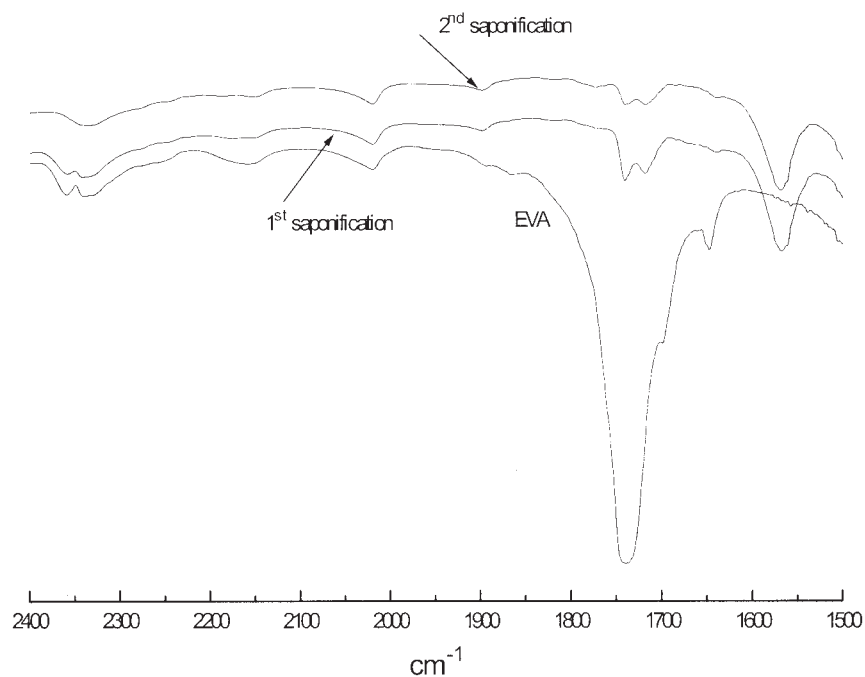


Figure 1 FTIR spectra of EVA19 and EVOH19.

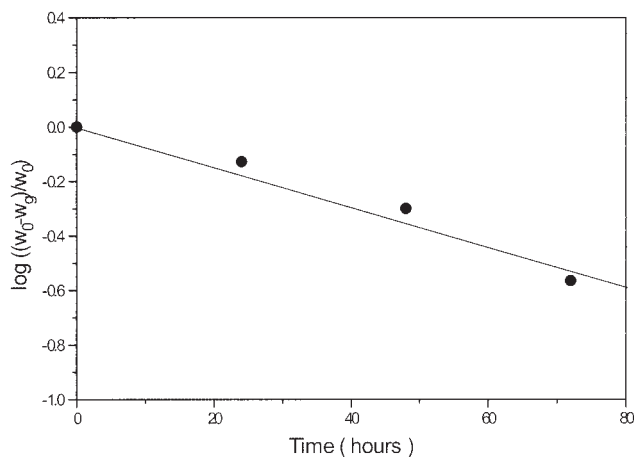


Figure 2 Logarithm of $(w_0 - w_g)/w_0$ versus time.

RESULTS AND DISCUSSION

Synthesis of EVOH-g-PCL

EVA19 was ground under cryogenic conditions and then saponified in 0.5 M KOH/ethanol at room temperature to produce poly(ethylene-co-19% vinyl alcohol) (EVOH19). Because both EVA19 and EVOH19 were not soluble in the reaction medium, the saponification reaction proceeded heterogeneously.

Fourier transform infrared (FTIR) spectra of EVA19 (Fig. 1) after saponification for 24 h indicated that some of the vinyl acetate units remained unsaponified because the C=O stretching band still appeared at $1650\text{--}1775\text{ cm}^{-1}$. This was because the saponification took place preferentially at the surface of the EVA19 particles and allowed EVA19 molecules inside the particles to remain almost intact.¹²

The saponified EVA19 powder was dissolved in hot toluene and precipitated in methanol. The precipitated lump was ground and saponified again. The peak at $1650\text{--}1775\text{ cm}^{-1}$ was greatly weakened, and the peak intensity was less than 1% of that corresponding to pristine EVA19 after two saponifications.

CL was ring-opening-polymerized with EVOH19 synthesized by two saponifications of EVA19. The ring-opening polymerization of CL proceeded so slowly that the concentrations of PCL grafted from EVOH19 were 15.6, 25.7, and 35.8 wt % after 24, 48, and 72 h of the reaction, respectively.

Figure 2 plots $\log[(w_0 - w_g)/w_0]$ as a function of the polymerization time; w_0 and w_g are the initial amount of CL in the reaction medium and the amount of grafted PCL, respectively. The linear relationship in Figure 2 indicates that the ring-opening polymerization followed first-order kinetics with respect to the CL concentration, even though a small amount of the PCL homopolymer was produced as a byproduct.

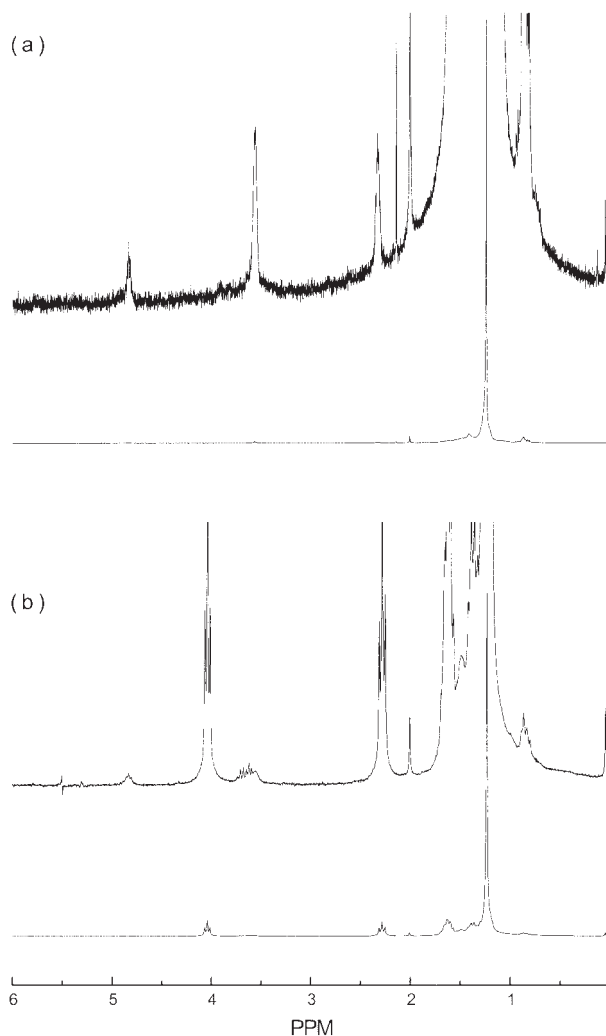


Figure 3 $^1\text{H-NMR}$ spectra of (a) EVOH and (b) EVOH-g-PCL19.

Figure 3 presents $^1\text{H-NMR}$ spectra of EVOH19 and EVOH19-g-PCL. The peaks at 4.0–4.2 ppm were assigned to the methylene protons of PCL next to ester bonds, and this allowed the determination of the composition of the graft copolymers. The peaks at 3.6 ppm were assigned to the methine protons of vinyl alcohol

TABLE III
Composition of the Synthesized EVOH-g-PCL

Sample code	<i>a</i>	<i>b</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	DP_w^a
EVOH	0.891	0.109	0.0733	0.0357			
EVOH-g-PCL16	0.891			0.0357	0.0164	0.0569	0.901
EVOH-g-PCL26	0.891			0.0357	0.0158	0.0575	1.516
EVOH-g-PCL36	0.891			0.0357	0.0146	0.0587	2.403

^a As determined by eq. (4).

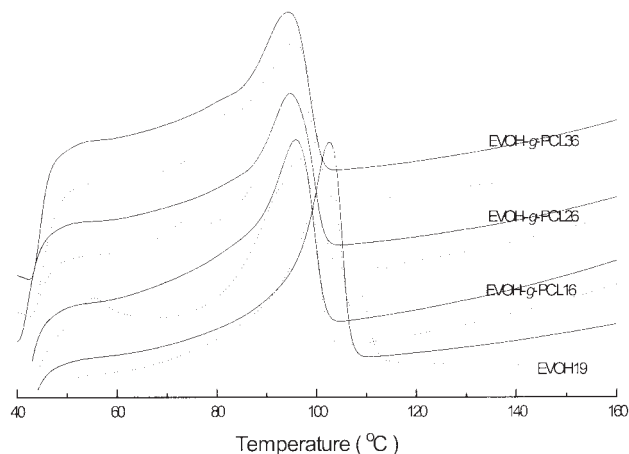


Figure 4 (· · ·) First scan and (- - -) second DSC scan thermograms of EVOH-g-PCL.

(VOH) units that remained intact after the graft copolymerization. The weight-average degree of polymerization of PCL branches (DP_w) for EVOH-g-PCL was determined from the weight increase (Δw) due to the graft copolymerization:

$$DP_w = \frac{\Delta w \times M_0}{114 \times w \times x} \quad (4)$$

where w is the weight of the macroinitiator (EVOH19), x is the molar fraction of VOH units that reacted with CL (Table III), and M_0 is the average molar mass of the repeating unit of EVOH19 ($0.891 \times 28 + 0.0733 \times 46 + 0.037 \times 86$).

According to Table III, more than 75% of the VOH units vanished at an early stage of the graft copolymerization (before 24 h). Afterwards, the concentration of the unreacted VOH units decreased very slowly with time, even though the graft copolymerization proceeded homogeneously, because both EVOH19 and EVOH-g-PCL were soluble in the reaction medium.

The ring opening of CL could take place both at the hydroxy groups of units and at the chain-end hydroxy groups of grafted PCL branches. CL was ring-opened at pristine VOH units at an early stage of the polymeriza-

tion. As DP_w increased much more quickly at a later stage of the polymerization than the concentration of pristine VOH units decreased, we concluded that the chain-end hydroxy groups of grafted PCL branches, that is, the primary hydroxy groups, reacted with CL more quickly than the hydroxy groups of the pristine VOH units, that is, the secondary hydroxy groups.

Thermal properties of EVOH-g-PCL

Figure 4 shows DSC thermograms of EVOH-g-PCL. EVOH19 exhibited bimodal melting peaks at 102.6 and 108.5°C in the first DSC scan thermogram. The small higher temperature peak was attributed to less perfect crystals melting and recrystallizing during the heating scan. In the second DSC scan, which was obtained via reheating at 20°C/min after cooling from 200 to 30°C at -5°C/min, the higher temperature melting peak disappeared because crystallization was accomplished fully enough during the cooling step that the melting and recrystallization took place during the reheating step almost undetectably.

The first DSC scan thermogram of EVOH-g-PCL16, containing 15.6 wt % PCL, showed a small endothermic peak at 55°C. EVOH-g-PCL26 and EVOH-g-PCL36, containing 25.7 and 35.8 wt % PCL, respectively, exhibited corresponding melting peaks at 73 and 80°C, respectively. According to Table III, PCL branches in EVOH-g-PCL were not long enough to crystallize themselves. The small melting peaks did not originate from the melting of the PCL branches in EVOH-g-PCL because they were noticeably higher than the melting peak temperature (T_m) of the PCL homopolymer. The small endothermic peak moved to a higher temperature region as the PCL concentration increased, even though the PCL branches in EVOH-g-PCL should have impeded the crystallization of the EVOH moiety.

In the second DSC scan, the small endothermic peak disappeared for all three graft copolymers.

T_m of the EVOH19 moiety decreased as CL was grafted from EVOH19.

The PCL concentration of PCL-g-PCL did not have a significant effect on T_m . This observation agrees with

TABLE IV
Weight Decrease of PCL, EVOH-g-PCL, and the LDPE/PCL Blend during the Soil Burial Test

Soil burial time (days)	Weight decrease (%)					
	15	30	45	60	75	90
PCL	1.96 ± 0.023	8.63 ± 0.023	15.5 ± 0.022	30.1 ± 0.022	79.5 ± 0.023	—
LDPE/PCL (64/36)	0.57 ± 0.022	2.81 ± 0.023	3.65 ± 0.023	4.52 ± 0.023	4.92 ± 0.023	5.30 ± 0.023
EVOH-g-PCL16	0.54 ± 0.024	0.97 ± 0.024	1.12 ± 0.025	1.23 ± 0.021	1.23 ± 0.024	1.30 ± 0.023
EVOH-g-PCL26	0.34 ± 0.025	0.94 ± 0.022	1.17 ± 0.023	1.19 ± 0.022	1.19 ± 0.021	1.20 ± 0.020
EVOH-g-PCL36	0.89 ± 0.023	0.93 ± 0.023	1.10 ± 0.021	1.20 ± 0.026	1.20 ± 0.025	1.20 ± 0.023
LDPE	0.01 ± 0.02	0.03 ± 0.021	0.03 ± 0.021	0.03 ± 0.023	0.03 ± 0.023	0.03 ± 0.023

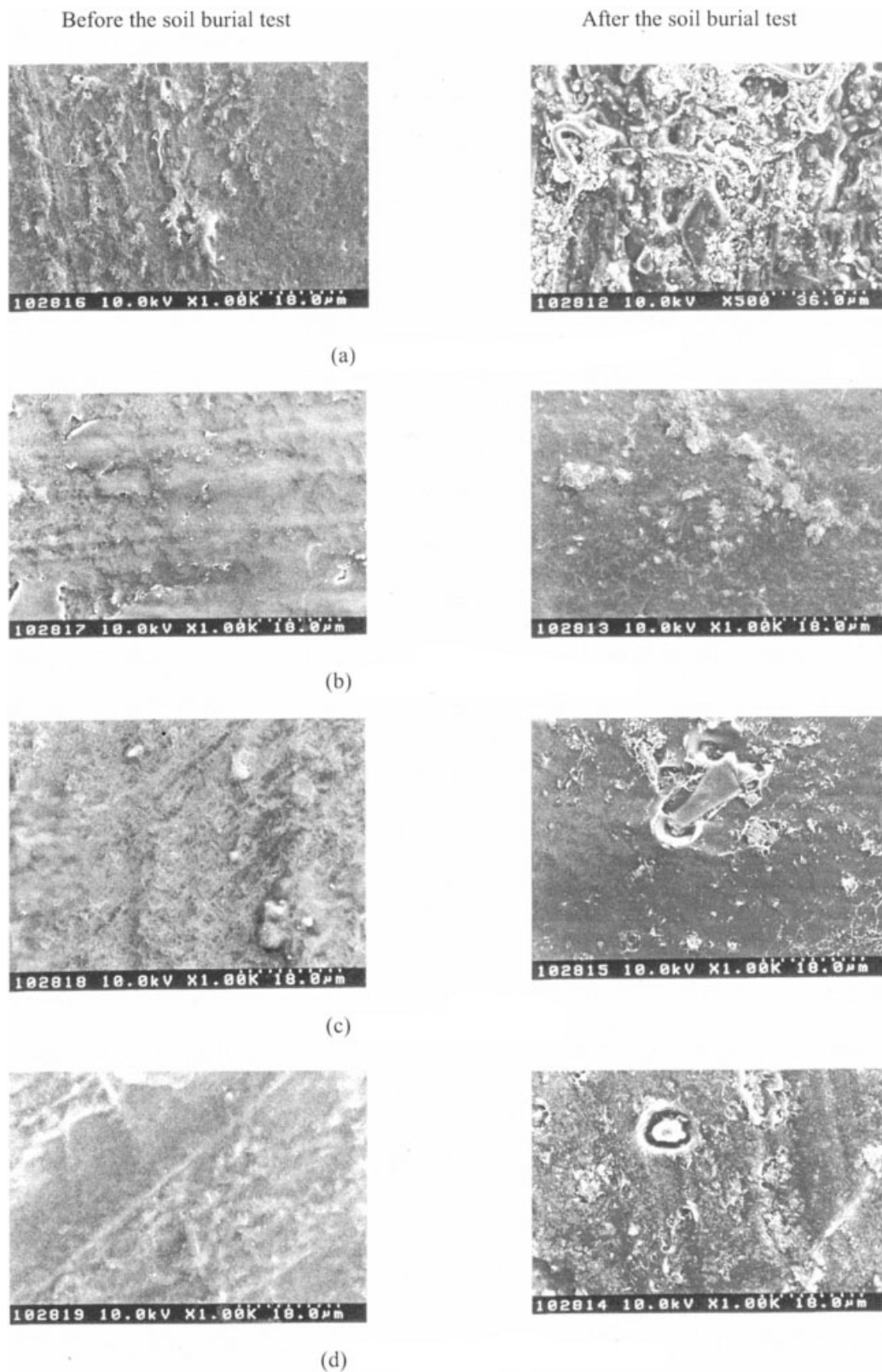


Figure 5 SEM micrographs of (a) LDPE/PCL (64/36), (b) EVOH-g-PCL16, (c) EVOH-g-PCL26, and (d) EVOH-g-PCL36 before and after 90 days of soil burial testing.

the results in Table III, in that the concentrations of the unreacted VOH units were not very different for the three graft copolymers, the PCL content of which was 15.6–35.8 wt %.

The crystallization of the crystallizable segments in EVOH-g-PCL depended on intermolecular interactions, which were governed principally by hydrogen bonds between vinyl alcohol (VOH) units. A reduction of intermolecular interactions between VOH units due to flexible PCL branches seemed to be insignificant and nearly independent of the length of the PCL branches when the concentration of VOH units remained invariable because EVOH and PCL were immiscible; as a result, the two components were almost completely phase-separated.

Soil burial test of EVOH-g-PCL

The weight reductions of the PCL homopolymer, a simple linear LDPE/PCL blend, and EVOH-g-PCL were measured as a function of time after they were buried in activated sludge soil, which was a heap of activated sludge from a municipal wastewater treatment plant.

Table IV shows that PCL degraded so quickly that PCL sheets were fragmented into invisibly small pieces after 90 days of the soil burial test. In contrast, the weight change of LDPE was negligible, as expected.

LDPE/PCL (64/36 w/w) lost much more weight than EVOH-g-PCL36, even though the two specimens contained similar amounts of PCL. However, the weight reduction of EVOH-g-PCL was nearly independent of the PCL concentration in the graft copolymers.

Figure 5 shows the surface morphology of LDPE/PCL and EVOH-g-PCL before and after 90 days of soil burial testing. The surface of the simple LDPE/PCL (64/36) blend was eroded much more than that of EVOH-g-PCL36, and this agreed with the weight-reduction results listed in Table IV.

The surface erosion of EVOH-g-PCL36 was more discernible than that of EVOH-g-PCL16 and EVOH-g-PCL26, even though the weight reductions of the three graft copolymers were similar, as shown in Table IV. These results indicate that the biodegradation of PCL occurred to a limited extent on the surfaces of the specimens, and PCL in the interior remained almost intact after 90 days of soil burial testing.

An accelerated hydrolysis experiment in a 0.1M KOH solution at 60°C for 1 week showed the same trend. A simple LDPE/PCL (64/36) blend showed a quite eroded and percolated morphology, as displayed in Figure 6.

Holes were not formed in EVOH-g-PCL until the PCL concentration was 35.6 wt %. Both EVOH-g-PCL 16 and EVOH-g-PCL26 were devoid of any eroded holes.

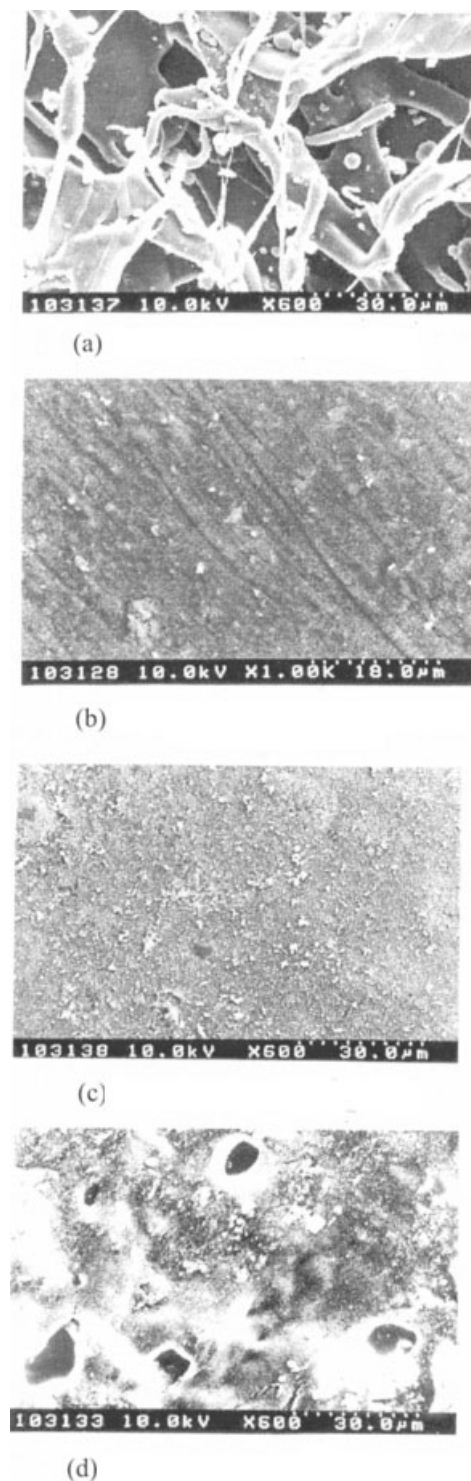


Figure 6 SEM micrographs of (a) LDPE/PCL (64/36), (b) EVOH-g-PCL16, (c) EVOH-g-PCL26, and (d) EVOH-g-PCL36 after hydrolysis.

Table V summarizes the tensile properties of PCL, an LDPE/PCL blend, and EVOH-g-PCL as a function of the soil burial time.

The elongation modulus and stress at the maximum load and the elongation at break of PCL decreased

TABLE V
Tensile Properties Before and After the Soil Burial Test

Sample code	Soil burial time (days)	Elongation modulus (MPa)	Stress at maximum load (MPa)	Elongation at break (%)
PCL	0	162.3 ± 26.0	12.7 ± 5.13	216.5 ± 35.9
	30	121.2 ± 21.5	6.82 ± 1.56	10.7 ± 4.96
	45	78.9 ± 32.7	3.22 ± 1.90	11.7 ± 5.25
LDPE/PCL 64/36	0	84.3 ± 15.2	4.38 ± 0.84	8.77 ± 1.36
	30	86.8 ± 9.30	4.26 ± 0.44	8.22 ± 1.58
	60	85.2 ± 12.3	3.68 ± 0.93	8.56 ± 3.25
	90	67.0 ± 12.4	3.06 ± 1.06	8.08 ± 2.68
EVOH-g-PCL16	0	34.7 ± 6.27	3.13 ± 0.60	32.7 ± 8.72
	30	31.3 ± 6.47	2.65 ± 0.53	31.8 ± 16.5
	60	30.6 ± 5.75	2.55 ± 0.78	23.9 ± 6.36
	90	28.3 ± 3.57	2.52 ± 0.55	23.5 ± 19.8
EVOH-g-PCL26	0	27.9 ± 5.28	2.61 ± 0.55	31.8 ± 10.5
	30	23.1 ± 3.34	2.43 ± 2.43	31.4 ± 11.5
	60	27.4 ± 4.41	2.69 ± 0.28	28.4 ± 13.8
	90	27.0 ± 5.85	2.64 ± 0.54	24.3 ± 10.9
EVOH-g-PCL36	0	33.5 ± 6.47	3.21 ± 0.53	94.8 ± 16.0
	30	28.5 ± 3.13	2.94 ± 0.44	89.1 ± 61.1
	60	26.7 ± 4.83	2.81 ± 0.40	55.7 ± 16.9
	90	26.2 ± 15.5	2.78 ± 1.28	21.9 ± 14.9
LDPE	0	56.9 ± 7.50	10.4 ± 1.20	476.1 ± 16.2

precipitously, and this indicated that PCL degraded very quickly. The flexibility and ductility of EVOH-g-PCL increased with an increase in the PCL concentration, and the elongation modulus of EVOH-g-PCL36 was lower than that of the LDPE/PCL (64/36) blend; however, the elongation at break of the former polymer was 10 times higher than that of the latter one.

The elongation at break of EVOH-g-PCL with a higher PCL concentration decreased more quickly, but it decreased to an asymptotic value of approximately 20%, regardless of the PCL concentration, as the soil burial time increased.

The elongation at break of LDPE/PCL (64/36) was as low as 8.8%, but it decreased little even after 90 days of soil burial testing. In sharp contrast, the elongation at break of EVOH-g-PCL36 were as high as 95% initially, but it decreased to 22% after 90 days of soil burial testing. Nevertheless, according to Table IV, the weight loss of the simple LDPE/PCL (64/36) blend was much more significant than that of EVOH-g-PCL36.

As shown in Figure 6, PCL and LDPE in the simple LDPE/PCL (64/36) blend constituted a dispersed phase and a continuous one, respectively. As PCL was incompatible with LDPE, the interaction between PCL and LDPE phases should have been so weak that the elongation at break of an LDPE/PCL blend depended mainly on the continuous LDPE phase. The degradation of PCL left the network structure of the continuous LDPE phase intact, and so it did not reduce the elongation at break of the blend appreciably.

On the other hand, PCL in EVOH-g-PCL was chemically bonded to EVOH. Therefore, the PCL moiety should have been well dispersed in EVOH-g-PCL, and the mechanical properties of the graft copolymer de-

pended on the small PCL branches as well as the EVOH moiety.

Table IV reveals that EVOH-g-PCL lost less than 1.3% of its weight after 90 days of soil burial testing. Moreover, surface erosion was not very significant after the soil burial test or after the accelerated hydrolysis. The rapid decrease in the elongation at break of EVOH-g-PCL with the soil burial time was ascribed to abiotic hydrolysis of PCL branches because microorganisms themselves or exoenzymes secreted by microorganisms could hardly reach the finely dispersed PCL moiety embedded in the EVOH matrix.

References

1. Rehm, K. E. Proceedings of the 4th International Conference on Biomaterials; Denkendorf, Germany: 1992; p 163.
2. Nakamura, T.; Shimizu, Y.; Matsui, T.; Okumura, N.; Hyan, S. H.; Nishiya, K. Proceedings of the 4th International Conference on Biomaterials; Denkendorf, Germany: 1992; p 153.
3. Li, G.; Cai, Q.; Bei, J.; Wang, S. *Polym Adv Technol* 2003, 14, 239.
4. Liu, S. J.; Ueng, S. W.; Chan, E.-C.; Lin, S.-S.; Tsai, C.-H.; Wei, F.-C.; Shih, C.-H. *J Biomed Mater Res* 1999, 48, 613.
5. Furukawa, T.; Matsusue, Y.; Yasunaga, T.; Nakagawa, Y.; Okada, Y.; Shikinami, Y.; Okuno, M.; Nakamura, T. *J Biomed Mater Res* 2000, 50, 410.
6. Cordewener, F. W.; Dijkgraaf, L. C.; Ong, J. L.; Agrawal, C. M.; Zardeneta, G.; Milam, S. B.; Schmitz, J. P. *J Biomed Mater Res* 2000, 50, 59.
7. Andreopoulos, A. G. *Clin Mater* 1994, 15, 89.
8. Riley, R. T. *J Agric Food Chem* 1983, 31, 202.
9. Stout, E. L.; Doane, W. M. *J Appl Polym Sci* 1979, 24, 153.
10. Scheiber, M. M.; White, M. D. *Weed Sci* 1980, 28, 685.
11. Chemical Economics Handbook; SRI International: Stanford, CA, 1981; p 8001.
12. Park, E. S.; Kim, M. N.; Yoon, J. S. *J Polym Sci Part B: Polym Phys* 2002, 40, 2561.