Synthesis and Biodegradation of Starch-Graft-Poly(hexylene adipate)

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ABSTRACT: Poly(hexylene adipate) (PHA) was synthesized by the direct condensation of hexandiol and adipic acid with *p*-toluene sulfonic acid as a catalyst, dimethyl benzene as a solvent. The terminal carboxyl group of the polyester was then converted to acyl chloride by a solution of $SOCl_2$ in toluene. The degree of acylation (DA) was very much dependent on the molecular weight and the type of the other terminal group of the PHA (hydroxyl or capped with an ester group). A high concentration of $SOCl_2$ increased DA, but the scission of the polyester chain was observed. The graft reaction of the acylated PHA with starch was carried out in dried dimethyl sulfoxide. The results show that the percentage grafting (*G*) and graft efficiency were determined by several factors, including the weight ratio of the reactants, reaction temperature, and molecular weight of PHA. Biodegradation tests in both the laboratory and the natural environment indicated that the degradation rate of starch-*g*-PHA was much faster than that of PHA. For example, the weight loss of PHA was 1.3% after 36 days of natural soil burial, whereas the weight loss of starch-*g*-PHA (*G* = 39.1%) reached 28% after the same time period. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 848–854, 2003

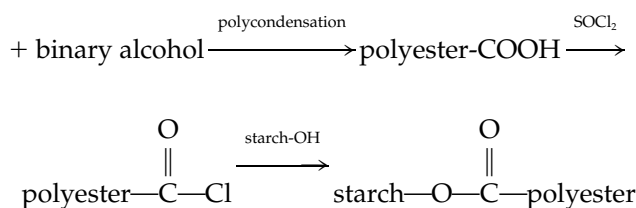**Key words:** polycondensation; graft copolymers; biodegradable

INTRODUCTION

With the increasing use of one-off plastic products, environmental pollution resulting from plastic waste has become more and more serious. Many scientists have focused their attention on the development of biodegradable polymers to substitute unbiodegradable polymers in the manufacture of disposable products. Because of the good biodegradability and low price of starch and aliphatic polyesters, many investigation have been conducted on producing blends of starch and polyesters.[1–6] However, because of the poor compatibility of these two components, the starch or the polyester must be first chemically modified before blending, or a large quantity of a compatible agent has to be used. On the basis of this background, some researchers have done work on the synthesis of starch-graft-polyesters. For example, Mani et al. grafted polycaprolactone (PCL) onto starch through the reaction of isocyanate-terminated PCL with starch and used it as a compatibilizer in a starch/PCL blend.[7] Kweon et al. also prepared starch-*g*-PCL through the reaction of diisocyanate-terminated PCL with starch, and the thermal characteristics of the copolymer was studied.[8] Tanaka et al. prepared a polyester-grafted starch–polymer alloy by the ring-opening graft polymerization of lactone and by the subsequent addition of an esterifying agent to simultaneously esterify the hydroxyl groups at the terminal of the polyester chain and in the starch molecule. This alloy has the potential to make plastic materials.[9] Recently, Kweon and Lim again reported work on the synthesis of starch-*g*-PCL via the chlorination of starch, followed by a reaction with the hydroxyl group of the PCL terminal. This PCL-substituted starch displayed good water resistance.[10] In our laboratory, starch-*g*-poly(lactic acid) was synthesized by the ring-opening graft polymerization of DL-lactide onto starch. This polyester-grafted starch also displayed good water resistance and good biodegradability.[11,12]

In this article, we report a new route for the synthesis of a starch-graft-polyester. This route is simply described as follows:

binary acid

$$\text{+ binary alcohol} \xrightarrow{\text{polycondensation}} \text{polyester-COOH} \xrightarrow{\text{SOCl}_2}$$

$$\underset{\text{polyester}}{\overset{\displaystyle \overset{\textstyle O}{\overset{\|}{}}}{}} \!\!\!-\!\!C\!-\!Cl \xrightarrow{\text{starch-OH}} \text{starch}-O-\overset{\overset{\textstyle O}{\|}}{C}-\text{polyester}$$

This route offers great variability in the synthesized starch-graft-polyester because there are a lot of monomers available and they are relatively cheap. The structure of the polyester could be designed by vari-

ation of the binary acid and binary alcohol, and the molecular weight could be controlled in the polycondensation. The percentage grafting (*G*) of the starch graft polyester also could be controlled in the graft reaction. It is very promising that the graft copolymer can be created with tailor-made properties. In this work, we synthesized poly(hexylene adipate) (PHA) and grafted it onto corn starch. The factors that influenced the graft reaction were studied. The biodegradation behaviors of PHA and starch-*g*-PHA were also investigated.

EXPERIMENTAL

Materials

Adipic acid, 1,6-hexandiol, and *p*-toluene sulfonic acid were all analytical grade and were received from Shanghai Chemical Co. (China). Dimethyl benzene, *n*-butyric acid, and ethyl acetate were also analytical grade and were supplied by Tianjin Chemical Co. (China). All of these reagents were used as received. Dimethyl sulfoxide (DMSO) was received from Tianjin Chemical Co. and was dried by dimethyl benzene azeotropic distillation before use (the water was separated through a fractionation condenser). Corn starch (70% amylopectin and 30% amylose) was supplied by Tianjin Tianyuan Starch Plant (China) and was vacuum-dried before use.

Synthesis of PHA

PHA was synthesized from equivalent moles of 1,6-hexandiol and adipic acid in the presence of 0.4 mol % *p*-toluene sulfonic acid. Dimethyl benzene was used as a solvent. The reaction proceeded at the refluxing temperature of dimethyl benzene (~143°C) under a nitrogen atmosphere with continuous agitation. The azotrope of dimethyl benzene and water was condensed and passed through a 4A molecular sieve and then returned to the reaction flask. At certain time intervals, samples were taken out of the contents of the flask and were cast onto a watch glass and then vacuum-dried. We determined the number-average molecular weight (M_n) of each sample by dissolving it in ethyl acetate and then titrating it with a standard KOH ethanol solution. M_n was calculated as follows:

$$M_n = \frac{W}{C \times V}$$

where *W* is the weight of the polyester and *C* and *V* refer to the molar concentration and volume of the KOH solution, respectively. The degree of polymerization (X_n) and the extent of the reaction (*P*) were calculated according to the following equations:

$$X_n = \frac{M_n}{114} \quad P = 1 - \frac{1}{X_n}$$

where 114 is the average molecular weight of the structural unit of PHA. When it was necessary, on completion of the polycondensation excess *n*-butyric acid was added, and the reaction proceeded for another 3 h. Thus, the hydroxy terminal of the polyester was capped by a butyric ester. Finally, the polyester was precipitated by ethanol and recovered by filtration.

Acylation of the carboxy terminal of PHA

Dried PHA was first dissolved in toluene, and then, $SOCl_2$ was added. The reaction was carried out at 50°C in a four-necked flask equipped with a condenser (attached with a dry tube), a thermometer, an agitator, and a nitrogen inlet. The side products HCl and SO_2 were absorbed by the NaOH solution. At the end of the reaction, vacuum distillation was used to remove the excess $SOCl_2$. Then, the acylated polyester was precipitated with petroleum ether (60–90°C) and vacuum-dried. The content of the acyl chloride group was measured by hydrolysis of the acyl chloride group in a sealed apparatus followed by electrometric titration with $AgNO_3$ solution as a titrant. The degree of acylation (DA) was calculated as follows:

$$DA\ (\%) = \frac{\text{mole of acyl chloride group of the product}}{\text{mole of carboxyl group of PHA}}$$

Graft reaction of starch with acylated PHA

Acylated PHA and starch were first dissolved in dried DMSO and were then mixed in a four-necked flask, which was equipped with a condenser (attached with a dry tube), a thermometer, an agitator, and a nitrogen inlet. A small amount of triethyl amine was added as a catalyst. The flask was then heated to the desired temperature, and the reaction proceeded for a designed time. Then, the contents of the flask were precipitated with ethanol, and the product was vacuum-dried.

Determination of *G* and graft efficiency (GE)

The dried graft product (2 g) was placed in a Soxhlet's extractor and extracted with toluene for 24 h to remove the ungrafted polyester. After it was vacuum-dried, the residue was put in a conical flask containing 100 mL of 1 mol/L HCl and refluxed for 1 h to hydrolyze the starch chain in the starch-*g*-PHA. After filtration, the residue (the graft chain) was vacuum-dried. *G* and GE were calculated as follows:

	Time (h)							
	2	5	10	15	20	25	30	35
M_n	1,130	6,120	9,320	12,390	15,830	19,160	20,020	20,030
X_n	9.894	53.69	81.75	108.7	138.9	168.1	175.6	175.7
P (%)	89.89	98.14	98.78	99.08	99.28	99.41	99.43	99.43

$$G\ (\%) = \frac{\text{weight of the graft chain}}{\text{weight of the graft product (2 g)}} \times 100\%$$

$$GE\ (\%) = \frac{G}{G_{th}} \times 100\%$$

where G_{th} is the theoretical percentage grafting, which was determined by the following equation:

$$G_{th} = \frac{\text{weight of acylated PHA} \times DA}{\text{weight of starch} + \text{weight of acylated PHA}}$$
$$\times 100\%$$

IR measurement

The IR spectrum of starch and the starch-*g*-PHA were measured with a Bio-Rad FTS 135 IR spectrometer (Japan).

Biodegradation tests

Biodegradation tests in the laboratory were carried out with 1-mm films of PHA or starch-*g*-PHA. The films were cut to pieces about 0.5 g in weight. Each piece was exposed to an aerated medium, which was composed of 100 mL of H_2O, 1 g of peptone, 0.5 g of beef extract, 0.5 g of NaCl, and *Bacillus subtilis.* The pH of the medium was adjusted to 7 by NaOH solution. The biodegradation temperature was kept at 37°C. The outdoor biodegradation tests were carried out by the burial of film pieces in natural soil at a depth of 20 cm. The samples were taken out of the environment at specific times, gently washed, dried, and weighed. The weight loss was recorded.
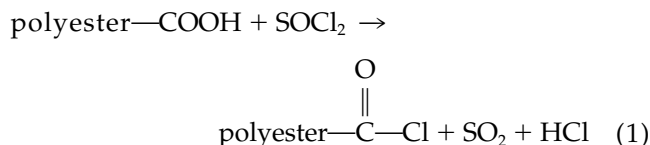
RESULTS AND DISCUSSION

Synthesis of PHA

Table I shows the kinetic results of the polycondensation of equimolar adipic acid and hexandiol in the presence of 0.4 mol % *p*-toluene sulfonic acid as a catalyst. To minimize the volatilization loss of the monomers, the condensation commenced at a relatively low temperature (110°C). As shown in Table I, after 2 h X_n had reached 9.894, and P had reached 89.89%. This indicates that most of the monomers had
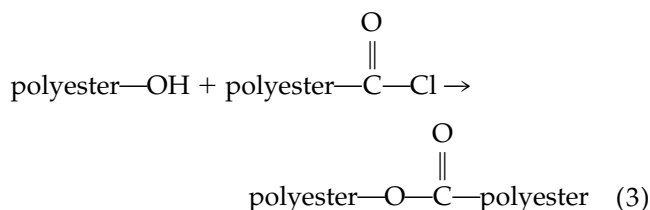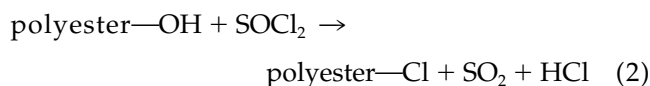
converted to oligomers. Then, the temperature was raised to 143°C, at which point the solvent, dimethyl benzene, boiled, and the byproduct, water, was removed from the reaction content successively by the azotropic distillation of dimethyl benzene with water. As shown in Table I, X_n and P increased dramatically and reached 53.69 and 98.14%, respectively, when the reaction time reached 5 h. After 5 h, X_n and P further increased with reaction time and reached 168.1 and 99.41%, respectively, at 25 h. After that, the polycondensation demonstrated a very slow rate and nearly reached an equilibrium state after 30 h. This means that the water could not be further removed under these polymerization conditions. According to these kinetic results, we synthesized PHA with different molecular weights by controlling the reaction times for subsequent study on acylation and the graft reaction.

Acylation of the carboxyl terminal of PHA

A solution of $SOCl_2$ in toluene was used to convert the carboxyl terminal of PHA to an acyl chloride terminal. The predominating reaction is

$$\text{polyester—COOH} + SOCl_2 \rightarrow$$

$$\begin{array}{c} O \\ \parallel \\ \text{polyester—C—Cl} + SO_2 + HCl \quad (1) \end{array}$$

The side reactions are

$$\text{polyester—OH} + SOCl_2 \rightarrow$$

$$\text{polyester—Cl} + SO_2 + HCl \quad (2)$$

$$\begin{array}{c} O \\ \parallel \\ \text{polyester—OH} + \text{polyester—C—Cl} \rightarrow \end{array}$$

$$\begin{array}{c} O \\ \parallel \\ \text{polyester—O—C—polyester} \quad (3) \end{array}$$

Equation (2) is not a harmful reaction when excess amounts of $SOCl_2$ are used because the Cl terminal will not affect the subsequent graft reaction of acyl

TABLE II
Results of the Acylation of PHA at 50°C

Entry	PHA terminal	PHA M_n	Concentration of $SOCl_2$ (%)	Time (h)	DA (%)	Acylated PHA M_n
1	HO~C(=O)—OH	17,365	16.7	5	27.4	17,362
2	HO~C(=O)—OH	17,365	28.6	5	47.3	17,358
3	HO~C(=O)—OH	17,365	50.0	5	50.6	17,355
4	HO~C(=O)—OH	17,365	70.0	5	64.3	14,238
5	HO~C(=O)—OH	17,365	100	5	77.2	8,328
6	C_3H_7—C(=O)—O~C(=O)—OH	17,365	50.0	5	60.3	
7	C_3H_7—C(=O)—O~C(=O)—OH	17,365	50.0	2	40.8	
8	C_3H_7—C(=O)—O~C(=O)—OH	17,365	50.0	4	50.2	
9	C_3H_7—C(=O)—O~C(=O)—OH	17,365	50.0	6	48.2	
10	C_3H_7—C(=O)—O~C(=O)—OH	12,139	50.0	5	66.8	
11	C_3H_7—C(=O)—O~C(=O)—OH	7,298	50.0	5	77.6	
12	C_3H_7—C(=O)—O~C(=O)—OH	3,728	50.0	5	82.8	

chloride with the hydroxyl groups in the starch molecule. Equation (3) is an undesired reaction because it not only causes chain extension or chain cyclization, but it also causes the loss of acyl chloride groups and, thus, will affect the subsequent graft reaction with starch. To minimize this side reaction, a relatively low temperature (50°C) was used in all of the experiments. Table II lists the results of the acylation of PHA on various conditions when the temperature was kept at 50°C. The first parameter studied was the concentration of $SOCl_2$. An examination of entries 1–5 in Table II indicates that DA increased with increasing $SOCl_2$ concentration. However, when the concentration of $SOCl_2$ was higher than 70%, the molecular weight of the polyester decreased after the acylation. This means that some chain scission occurred under these conditions. This was most probably caused by the attack of $SOCl_2$ on the ester bond:

$$\text{~C(=O)—O~} + \text{Cl—SCl} \rightarrow \text{~C(=O)—Cl} + \text{Cl—S—O~}$$
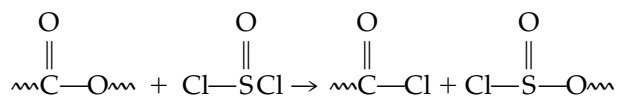
Considering both DA and molecular weight, we choose 50% $SOCl_2$ in the subsequent investigations. To prevent the side reaction shown in eq. (3), we used an excess amount of *n*-butyric acid (six times the moles of the hydroxyl groups) to cap the hydroxy terminal of the polyester on the completion of the polycondensation, and the reaction was prolonged for another 3 h. We did not find a proper method to evaluate the capping degree because the residual hydroxyl groups were too few. However, the results of subsequent acylation show that this was effective. DA increased from 50.6 to 60.3% (see entries 3 and 6 in Table II). We also studied the influence of reaction time. The results indicate that 5 h was a proper reaction time when the

TABLE III
Results of the Graft Reaction of Acylated PHA with Starch

Entry	PHA terminal	PHA M_n	PHA DA (%)	PHA/starch (w/w)	Temperature (°C)	Time (h)	G (%)	G_{th} (%)	GE (%)
1	HO~~C—Cl (C=O)	14,288	60.8	1/2	50	5	18.2	20.2	90.0
2	HO~~C—Cl (C=O)	14,288	60.8	1/1	50	5	23.1	30.4	76.0
3	HO~~C—Cl (C=O)	14,288	60.8	2/1	50	5	33.1	40.6	81.5
4	C_3H_7—C—O~~C—Cl (C=O, C=O)	12,139	66.8	1/2	50	5	20.3	22.2	91.4
5	C_3H_7—C—O~~C—Cl (C=O, C=O)	12,139	66.8	1/1	50	5	29.4	33.4	88.0
6	C_3H_7—C—O~~C—Cl (C=O, C=O)	12,139	66.8	2/1	50	5	39.8	44.5	89.4
7	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	1	25.8	40.2	64.0
8	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	2	33.3	40.2	82.8
9	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	3	34.5	40.2	85.8
10	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	4	34.1	40.2	84.8
11	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	5	34.3	40.2	85.3
12	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	50	6	34.1	40.2	84.8
13	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	65	3	39.1	40.2	97.3
14	C_3H_7—C—O~~C—Cl (C=O, C=O)	17,365	60.3	2/1	85	3	33.2	40.2	82.6
15	HO~~C—Cl (C=O)	19,000	58.1	1/2	50	5	8.2	19.3	42.5
16	HO~~C—Cl (C=O)	3,000	86.5	1/2	50	5	27.1	28.8	94.1

concentration of $SOCl_2$ was 50% (see entries 6–9 in Table II). Although at first the DA increased with time, when the time was over 5 h, it decreased. These data show that some side reactions, such as that shown in eq. (3), occurred. Entries 6, 10, 11, and 12 in Table II display the effect of molecular weight on the acylation. As expected, a higher DA was achieved when the polyester with a lower molecular weight was used. This is because the reaction content was less viscous

when the polyester possessed a low molecular weight, and hence, the diffusion of the reagents became easier.

Graft reaction of acylated PHA with starch

Table III lists the results of the graft reaction of acylated PHA with corn starch with triethyl amine as a catalyst. We used two parameters to characterize the graft reaction: G and GE. The first factor was the
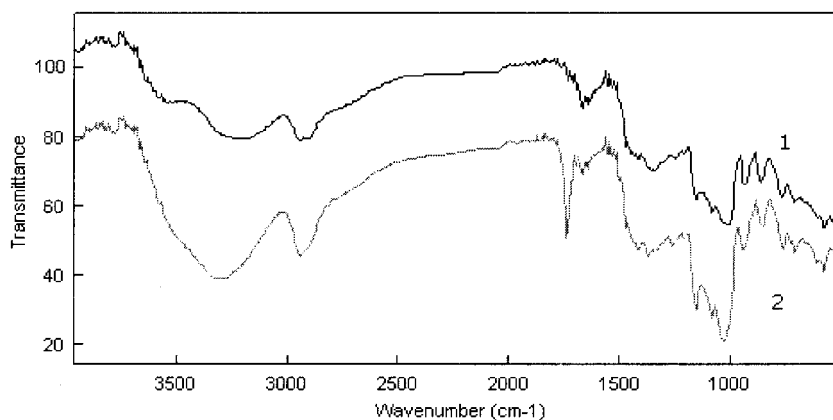
Figure 1 IR spectra of (1) starch and (2) starch-*g*-PHA (entry 13 in Table III).

weight ratio of PHA to starch. As expected, *G* increased with increasing weight ratio of PHA to starch. However, GE decreased a lot when the weight ratio was 1/1 or 2/1 (see entry 1–3). This was because the other terminal of the acylated PHA was a hydroxyl group. There was the possibility of the acyl chloride group reacting with the hydroxyl groups at the PHA terminal during the graft reaction. The more the polyester there is, the more the hydroxy terminal there is, and the more chances there are to react with the acyl chloride group. We verified this by capping PHA with an ester group to acylate it and then reacting it with the starch. In these cases, both *G* and GE were higher than that of not capped ones, and the GE did not decrease much with the increasing PHA (see entries 4–6 in Table II). Entries 7–12 in Table II demonstrate the influence of the reaction time on the graft reaction when the temperature was kept at 50°C and the weight ratio of PHA to starch was kept at 2/1. Before 3 h, both *G* and GE increased with reaction time. However, when the reaction time was greater than 3 h, *G* and GE did not changed obviously. This means that

the reaction of the acyl chloride groups with the hydroxyl groups was very quick and that 3 h was enough time. When the temperature was raised from 50 to 65°C, *G* increased from 34.5 to 39.1%, and GE increased from 85.8 to 97.3% (entries 9 and 13 in Table II). However, when the temperature was further raised to 85°C, *G* and GE decreased to 33.2 and 82.6%, respectively (entry 14 in Table II). This indicates that some side reactions occurred at higher temperatures. The influence of the molecular weight on the graft reaction was also studied. When the molecular weight of PHA decreased, both *G* and GE increased (see entries 11 and 6 in Table II). The lower the molecular weight of PHA was, the higher the *G* and GE were (see entries 15, 1, and 16 in Table II). We attributed this to the easy movement of smaller molecules, which increased the chance of collision of acyl chloride groups with starch hydroxyl groups.

Figure 1 shows the IR spectra of starch (curve 1) and starch-*g*-PHA (curve 2; sample 13 in Table III). Before the IR measurement, extraction was accomplished in a Soxhlet extractor to remove ungrafted polyester from
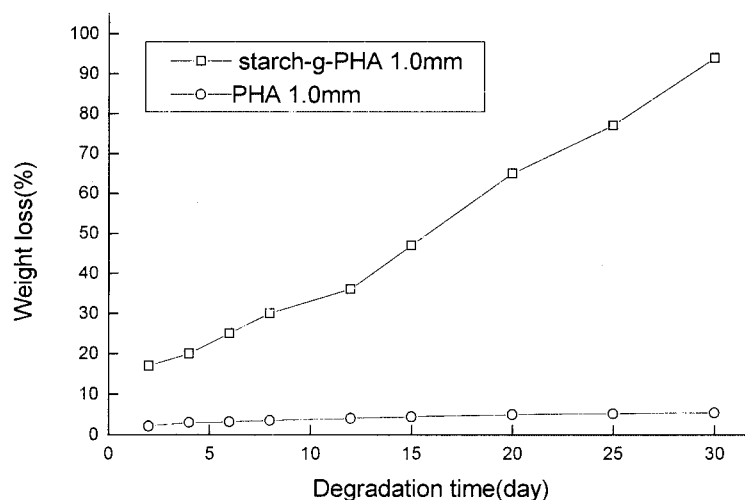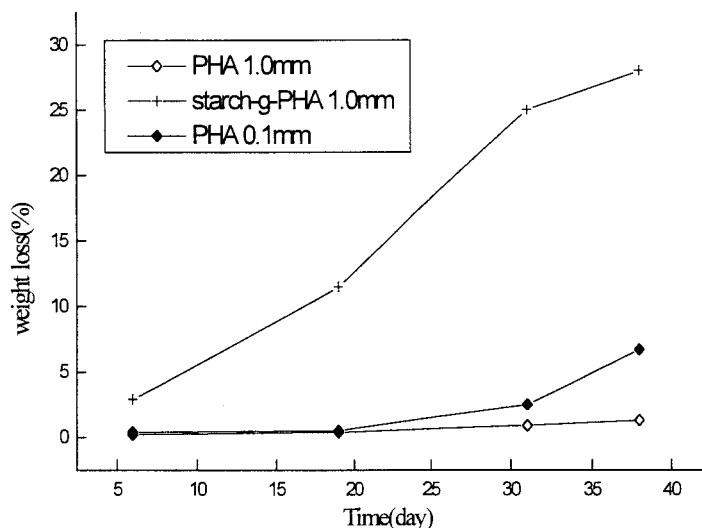

Figure 2 Weight loss of PHA (M_n = 17,365) and starch-*g*-PHA (*G* = 39.1%) in the presence of *Bacillus subtilis.*

Figure 3 Weight loss of PHA (M_n = 17,365) and starch-g-PHA (G = 39.1%) buried in natural soil.

the graft product with toluene as the extractant. Besides the enlarged peak at 1450 cm^{-1}, which originated from the CH$_2$ group in both the starch and polyester, there was a new peak at 1730 cm^{-1} in the spectrum of the starch-g-PHA, which characterized the carbonyl group in the polyester chain. These indicated that the polyester PHA had grafted onto the starch molecule.

Biodegradation behavior of PHA and starch-g-PHA

The biodegradation behavior of PHA (M_n = 17,365) and starch-g-PHA (G 39.1%) were investigated in the presence of *Bacillus subtilis. Bacillus subtilis* produces amylase during its growth, which is a specific catalyst for the degradation of starch. Figure 2 indicates that the degradation rate of starch-g-PHA was much faster than that of PHA. The weight loss reached 94% after 30 days, whereas the weight loss of PHA was only 5.4% after the same time period. Figure 3 shows the plot of weight loss versus degradation time for PHA and starch-g-PHA buried in natural soil. As shown, both PHA and starch-g-PHA exhibited environmental degradability. As in the laboratory, the graft copolymer displayed a faster degradation rate than the poly-

ester. The weight loss of the starch-g-PHA reached 28% after 36 days of burial, whereas the weight loss of PHA only reached 1.3% after the same time period. Figure 3 shows the influence of the film thickness on the degradation rate. When the PHA film was 0.1 mm thick, the weight loss reached 6.7% after 36 days of burial, which was much higher than that of 1.0 mm thick PHA film (1.3%).

References

1. Xu, W.; Doane, W.; Lawton J. Int Pat WO 97/44, 393 (1997).
2. Bastioli, C.; Bellotti, V. U.S. Pat. 5,412,005 (1995).
3. Bloembergen, S.; Marayan, B. US Pat 5,462,983 (1995).
4. Koenig, M. F.; Huang, S. J. Polymer 1995, 36, 1877.
5. Mani, R.; Bhattacharya, M. Eur Polym J 2001, 37, 515.
6. Kim, C. H.; Cho, K. Y.; Park, J. K. J Appl Polym Sci 2001, 81, 1507.
7. Mani, R.; Tang, J.; Bhattacharya, M. Macromol Rapid Commun 1998, 19, 283.
8. Kweon, D. K.; Cha, D. S.; Park, H. J.; Lim, S. T. J Appl Polym Sci 2000, 78, 986.
9. Tanaka, H.; Kawamatsu, T.; Utsue, I.; Okumura, Y.; Tanaka, H. U.S. Pat. 5,719,214 (1998).
10. Kweon, D. K.; Lim, S. T. J Appl Polym Sci 2001, 81, 2197.
11. You, Y.; Zhu, C.; Jiao, J.; Shen, X. Acta Polym Sinica 2000, 6, 746.
12. You, Y.; Shen, X.; Jiao, J.; Li, Z.; Zhu, C. Ion Exch Adsorption 2002, 18, 58.