Thermal Degradation and Biodegradability of Poly (lactic acid)/Corn Starch Biocomposites

Tsutomu Ohkita, Seung-Hwan Lee*

GreenBio Institute, 203 Oosakaya 295–1 Hanjyo-Cho Simogyo-ku, Kyoto 600-8433, Japan

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ABSTRACT: Thermal degradation and biodegradability of poly (lactic acid) (PLA) and poly (lactic acid)/corn starch (PLA/CS) composites with and without lysine diisocyanate (LDI) were evaluated by thermogravimetric analysis measurement and enzymatic degradation using Proteinase K and burial tests, respectively. Thermal stability was decreased by addition of CS and the composites with LDI showed higher thermal degradation temperature than those without LDI. In enzymatic biodegradation, the weight remaining of all samples decreased almost linearly with time. The addition of CS resulted in a faster rate of degradation and the composites with LDI were more difficult to degrade than those without it. In the composite without LDI, the degradation was faster at the interface between PLA and CS, showing deep and wide clearance, but degradation starting at the interface was not clearly observed in the composite with LDI. There was no considerable difference in molecular weight and distribution of the samples after enzymatic degradation. The lactic acid content of the water-soluble product obtained after enzymatic degradation increased with degradation time. In burial tests, pure PLA was little degraded but the composites gradually degraded. The degradation of the composite without LDI was faster than that of the composite with LDI. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3009–3017, 2006

Key words: thermal degradation; biocomposite; biodegradability; burial test; enzymatic degradation; poly (lactic acid); corn starch

INTRODUCTION

Biocomposites with natural resource fillers have become a major part of the biodegradable plastics industry, because natural resource fillers are abundant, inexpensive, renewable, and fully biodegradable raw materials.[1–6] Among these biocomposites, poly (lactic acid) (PLA)/corn starch (CS) composite has recently attracted attention as a fully bio-based biodegradable plastic.[7–9] PLA has many attractive features, such as good mechanical properties,[10,11] but is still more expensive than the conventional plastics. PLA can be easily degraded by enzymatic or alkali hydrolysis in compost, but its rate of degradation in soil is not good.[12–15]

CS is attractive from the standpoint not only of being a cheap filler, but also of providing excellent biodegradation properties to the final product. Therefore, biocomposting of PLA and CS is meaningful because starch can enhance the biodegradability of PLA in soil and reduce the total cost of the raw materials needed for the composite.

It is important to improve the interfacial adhesion between the component phases to obtain materials with satisfactory overall properties. We have developed a biocomposite from PLA and CS using lysine diisocyanate (LDI) as a coupling agent. In our previous report, it was found that the addition of LDI improved the mechanical properties and interfacial adhesion of the PLA and CS components.[16]

LDI is based on lysine with two amino and one carboxyl groups, which is one of the natural amino acids. LDI can react with hydroxyl or carboxyl groups in PLA, producing urethane bonds that can be easily and completely hydrolyzed into raw materials.[17–21] For example, the polyurethane that was synthesized from LDI, glycerol, and ascorbic acid can be completely degraded in aqueous solution and yielded nontoxic breakdown products such as lysine, glycerol, and ascorbic acid.[22] In fact, our interest in LDI as a bio-based coupling agent stems from these facts.

So far, several conventional isocyanates, such as methylene diisocyanate (MDI), toluene diisocyanate (TDI), 4,4′-methylenedicyclohexyl diisocyanate (hydrogenated MDI), and hexamethylene diisocyanate, have been used as a coupling agent.[22–27] For example, Wang et al. reported the effect of MDI on the properties of PLA/starch blend. The addition of MDI resulted in an enhancement of mechanical properties and water resistance.[28,29] However, these isocyanates

**Present address:* Tennessee Forest Product Center, 2506 Jacob Drive, University of Tennessee, Knoxville, TN 37996-4563.

Correspondence to: S.-H. Lee (Lshyhk@hotmail.com).

TABLE I
Composition of the Samples Used for Enzymatic Degradation and Burial Tests

Sample code	PLA/CS (wt %)	LDI (mL)
PLA	100/0	0
PLACS-1	90/10	0
PLACS-2	90/10	0.046
PLACS-3	70/30	0
PLACS-4	70/30	0.137
PLACS-5	50/50	0
PLACS-6	50/50	0.229

have found limited use as a biocompatible material because their ultimate hydrolysis products, i.e., their corresponding diamines such as 4,4′-methylenedianiline and 2,4-diaminotoluene, have been suspected to be cancer causing agents or produce hepatitis in man. So, nontoxic materials should be expected as a coupling agent, to synthesize fully biodegradable biocomposite without emitting toxic or noxious components.

This study aimed to evaluate thermal degradation and the biodegradability of the PLA/CS composite by thermogravimetric analysis (TGA) measurement and enzymatic degradation and burial testing, respectively. In particular, the effect of LDI addition was focused on.

EXPERIMENTAL

Materials

PLA (LACEA H-100J) and CS with 28% amylose were kindly supplied by Mitsui Chemicals Inc. (Tokyo, Japan) and Sanwa Cornstarch Co., Ltd. (Nara, Japan), respectively. LDI was kindly provided by Kyowa Hakko Co., Ltd. (Tokyo, Japan). Proteinase K from *Tritirachium album* was purchased from Nacalai Tesque Inc. (Kyoto, Japan). All other chemicals were purchased from commercial sources.

Preparation of biocomposites

The polymer and starch were first mixed as dry solids. The mixture was placed into a batch mixer (Labo Prostomill, Toyo Seiki Co., Ltd., Yamanashi, Japan) rotating at a speed of 30 rpm. After the addition, the rotation speed was increased to 70 rpm and kneading was conducted for 5 min. Then LDI was added to the mixture and kneading was further carried out for 10 min. The kneading temperature was 180°C. The kneaded samples were molded into sheets under a pressure of 150 kgf cm^{-2} at 180°C. The compositions of the samples obtained in this study and their sample codes are summarized in Table I.

Thermal degradation

TGA of the composites were performed with a Perkin–Elmer Pyris 1 TGA. Samples of 6–7 mg were heated from 50°C to 600°C at a rate of 10°C min^{-1} under nitrogen atmosphere (flow rate of 20 mL min^{-1}).

Enzymatic degradation test

The experiment was conducted with hot-pressed sheets ($10 \times 20 \times 0.4$ mm^3). Each of the samples was vacuum-oven dried overnight at 38°C and weighed. They were placed in a test tube and dipped in 5 mL of a Proteinase K solution (50 m*M* Tris-HCl buffer, pH 8.6). The concentration and enzyme activity of Proteinase K were 0.2 mg mL^{-1} and 15 U mg^{-1}, respectively. The test tube was sealed and kept at 37°C for a predetermined period and replaced every 48 h so that enzyme activity remained at a desired level throughout the experiment. The sample was then removed from the Proteinase K solution, washed thoroughly with distilled water and ethanol, and then dried *in vacuo* at 38°C. As a control, the same experiment was carried out without Proteinase K under the same conditions. The time course of the weight loss and enzymatic degradation was evaluated and the appearance of the samples was examined. To investigate the mechanism of degradation, the solution containing the portion degraded by the enzyme was analyzed by high performance liquid chromatography (HPLC).

Burial test

Hot-pressed sheets ($40 \times 10 \times 0.4$ mm^3) of pure PLA and PLA/CS composite were dried *in vacuo* for 24 h and weighed. They were buried in soil located in a room at 30°C and 80% relative humidity. The soil consisted of potting media, vermiculite, and composting microorganisms (Ihu Co., Aichi, Japan) in a weight ratio of 4:1:1. After each soil burial test for a week, the samples were washed and dried *in vacuo* at 38°C to constant weights. Then they were evaluated with regard to external appearance and weight loss.

Measurements

The average molecular weight (M_n and M_w) and polydispersity (M_w/M_n) of the samples after enzymatic degradation were determined by gel permeation chromatography (GPC). The GPC system consisted of a Shimadzu LC-10AD pump (Shimadzu Co. Ltd., Kyoto, Japan), a RID-10A RI detector (Shimadzu) and a SCL-10A controller (Shimadzu). A TSK-GEL G5000HHR column (φ 7.8 $\times$ 300 mm^2, Tosho Ltd., Tokyo, Japan) was used and chloroform was used as the eluent at a flow rate of 0.5 mL min^{-1} and at 40°C.

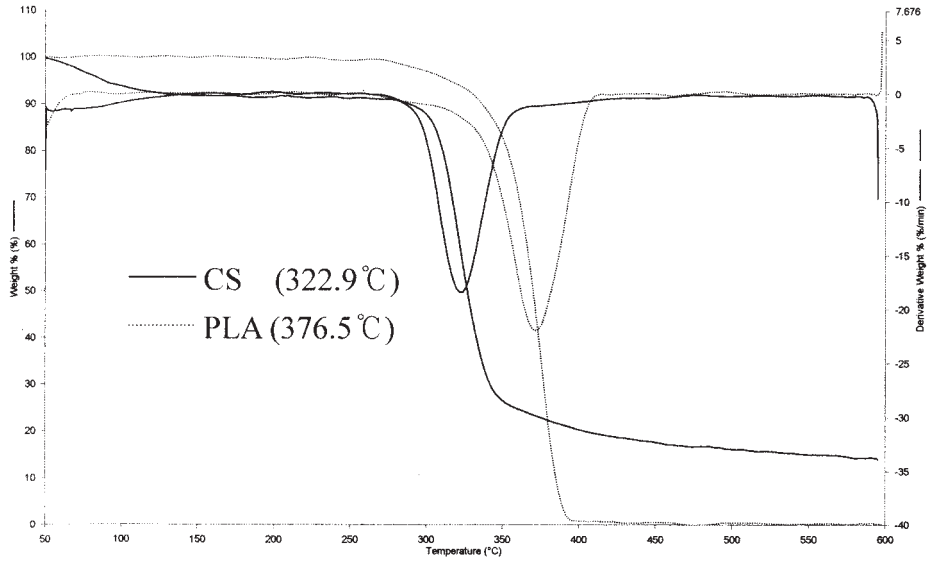

Figure 1 TGA and DTG thermograms of PLA and CS.

The molecular weight was calibrated to polystyrene standards.

The water-soluble products of the samples, after enzymatic degradation, were analyzed by HPLC to calculate the lactic acid (LA) content. The LA content was calculated using the following equation:

$$\text{LA content (\%)} = (\text{Weight of LA in water-soluble product} / \text{Weight of PLA in the sample}) \times 100 \quad (1)$$

HPLC was conducted with a system composed of two Shimadzu LC-10AD pumps and a Shimadzu SPD-10A UV–vis detector using a reversed-phase column of COSMOSIL $5C_{18}$-PAQ (φ 4.6 × 250 mm^2, Nacalai Tesque, Kyoto, Japan) to analyze the water-soluble products after enzymatic degradation. The sample was eluted with a 0.02*M* phosphate buffer solution at a flow rate of 0.5 mL min^{-1}.

The appearance of the samples after enzymatic and burial tests was investigated using a JEOL JSM-5900LV scanning electron microscope.

RESULTS AND DISCUSSION

Thermal degradation

Figure 1 shows the typical TGA and derivative thermograms (DTG) of PLA and CS. Complete thermal

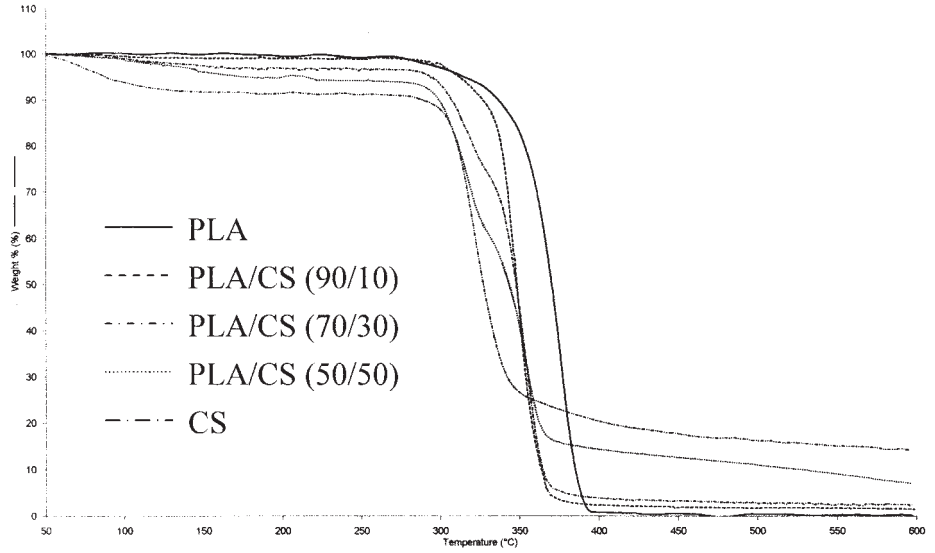

Figure 2 TGA thermograms for PLA, CS, and the composites with different CS content.

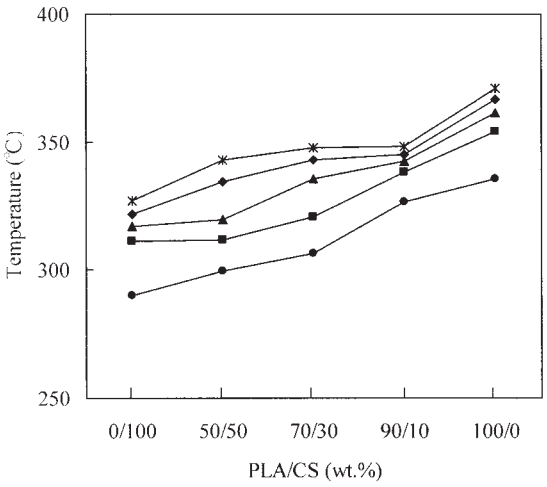

Figure 3 Temperature change at different loss of mass in PLA, CS, and their composites. (●)10%, (■) 20%, (▲) 30%, (♦) 40%, (*) 50% thermal degradation.

degradation of PLA and CS occurred in a single stage at 376.45°C and 322.9°C, respectively. Figure 2 shows the TGA curves for PLA, CS, and the 90/10, 70/30, and 50/50 (PLA/CS) composites with different CS content. The TGA curves of the composites showed a thermal stability intermediate to those of PLA and CS, and a two-stage loss of mass was observed for all composites. The first stage in the temperature range of 280–350°C is due to CS decomposition as it is similar to those of pure CS. The second one, appearing at higher temperatures in the range of 350°C and 400°C, corresponded to the thermal degradation of PLA. Increasing the CS content decreased thermal degradation temperature of the composites.

Figure 3 shows the temperatures at 10, 20, 30, 40, and 50% losses in mass for PLA, CS, and their composites. It was also found that an increase in CS content increased the loss of mass in the composite. Figure 4 shows the DTG thermogram of the PLA/CS (70/30) composites with and without LDI, showing the effect of LDI on the thermal degradation of the composites. The peak temperatures of first and second stages were 316°C and 352°C in the composite without LDI, respectively, whereas those were increased to 321.1°C and 378.6°C, respectively, with the addition of LDI. This may be explained by the fact that a graft copolymer of PLA and CS, a molecular chain-extended PLA, and crosslinked CS itself could be produced during the kneading at high temperature, as reported in our previous reports.[2,16] It can be generally said that the increase in PLA molecular weight and crosslinking reaction of CS could increase the thermal degradation temperature of PLA and CS, respectively.

The degradation temperature and percent weight loss for different thermal degradation steps and the percent ash content at 600°C for all samples are given in Table II. It was observed that the percent ash content increased from 2.1% to 8.1%, with an increase in starch from 10% to 50%. It may be due to the fact that the starch is a carbohydrate, which yields high charred products. There was no significant difference in ash content between the composites with and without LDI.

Enzymatic degradation

As Proteinase K easily degrades PLA, the biodegradability of pure PLA and PLA/CS composite with and without LDI was conducted by enzymatic degradation using Proteinase K.

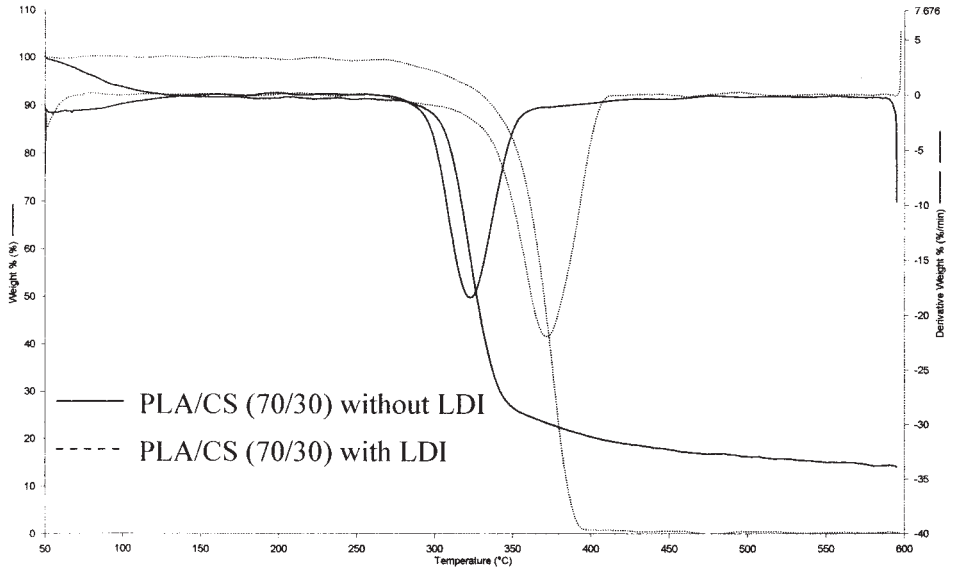

Figure 4 DTG thermograms of PLA/CS (70/30) composites with and without LDI.

TABLE II
Peak Temperature, Percent Degradation, and Ash Content at 600°C from DTG Analysis for PLA, CS, and Their Composites

Sample	Peak temperature (°C)	Degradation (%)	Ash content at 600°C (%)
PLA	376.5	77.3	0.5
PLA/CS (90/10) composite			
Without LDI	308.6	12.4	1.1
	348.7	52.9	
With LDI	312.6	13.7	1.2
	377.5	61.1	
PLA/CS (70/30) composite			
Without LDI	316.7	16.7	3.4
	352.2	61.3	
With LDI	321.1	16.3	3.7
	378.6	66.2	
PLA/CS (50/50) composite			
Without LDI	319.3	29.6	8.1
	371.4	73.0	
With LDI	319.5	21.7	7.9
	373.4	53.5	
CS	322.9	42.1	15.0

Figure 5 shows the weight remaining for pure PLA and PLA/CS composite with and without LDI of various compositions as a function of time. The samples were little degraded in the buffer solution without Proteinase K, showing less than 0.5% weight loss (data not shown). The remaining weight of all samples decreased almost linearly with time. The slopes were calculated from this linear relationship. The values obtained are indicated in Figure 5. The degradation of pure PLA was slower than that of any composites. Basically, a higher CS content resulted in a faster

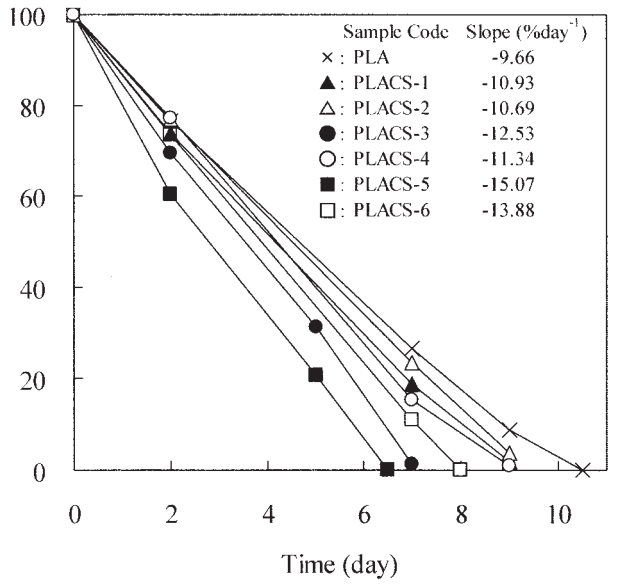

Figure 5 Weight remaining for pure PLA and PLA/CS composites with and without LDI plotted as a function of enzymatic degradation time.

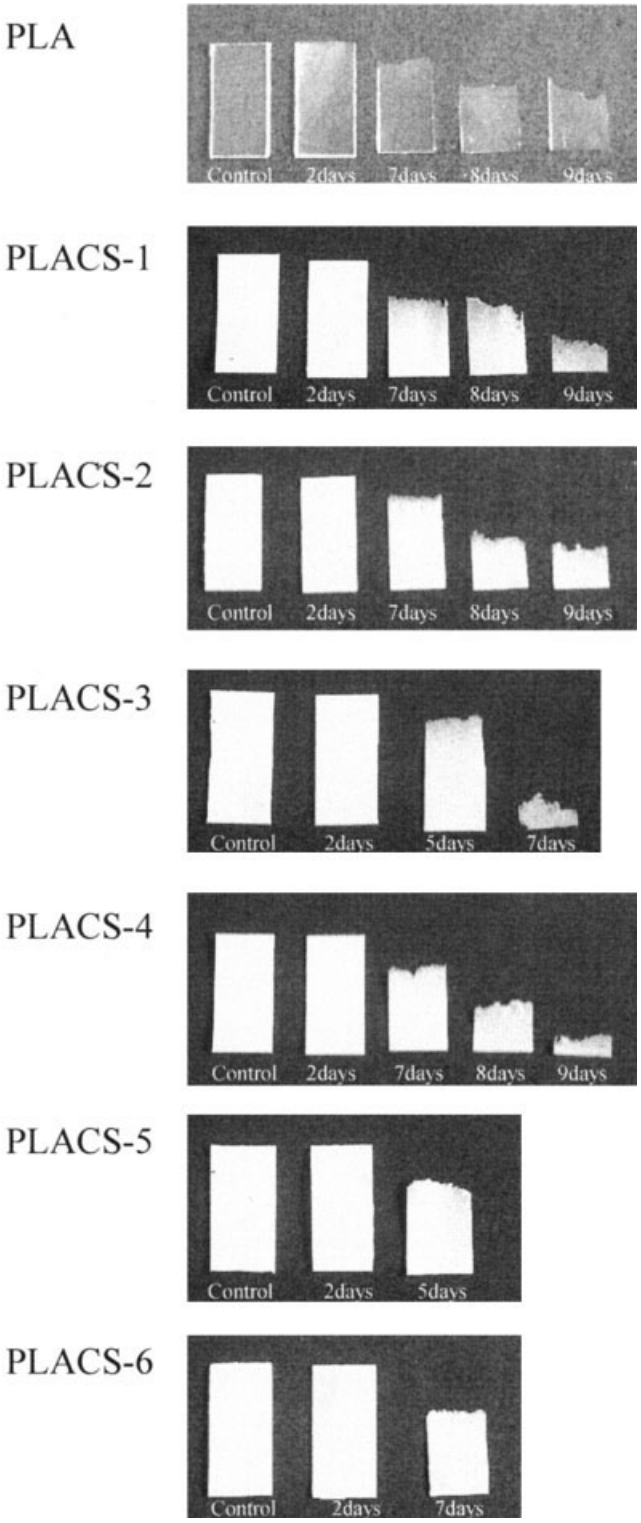

Figure 6 Photographs of pure PLA and PLA/CS composite with and without LDI before and after enzymatic degradation.

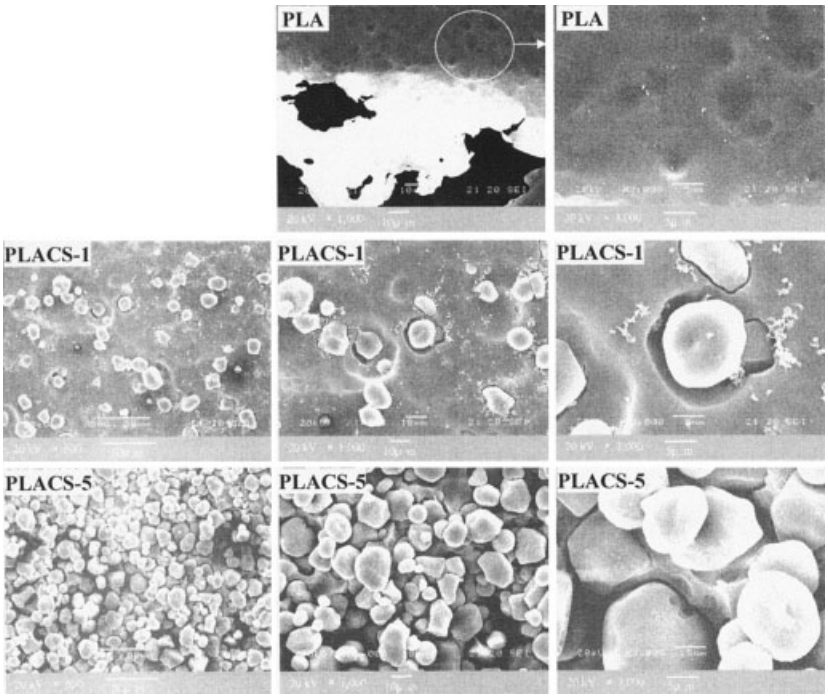

Figure 7 SEM micrographs of pure PLA and PLA/CS composite without LDI after enzymatic degradation. Sample code: PLA (8 days), PLACS1 (8 days), and PLACS5 (5 days).

degradation. PLA/CS (50/50) without LDI was degraded fastest of all the samples. This result may be attributed to the increased surface exposed to enzyme degradation. That is, because the interfacial area between CS and the PLA matrix and the discontinuity of the PLA matrix were increased by the increase in CS, the degradation rate increased for the composites with a higher content of CS.

The composites with LDI were more difficult to degrade than those without. As mentioned earlier, this may be attributed to the improved interfacial adhesion between CS and the PLA matrix due to the coupling effect of LDI. Stronger interfacial adhesion will reduce the area exposed to enzyme hydrolysis, resulting in a decrease in the degradation rate. The removal of hydroxyl groups of PLA and CS by LDI can also be considered a reason why the degradation of the composite with LDI was delayed. As reported in our previous paper,[16] LDI reacts with terminal hydroxyl and carboxyl groups of PLA and the hydroxyl groups of CS, producing three kinds of products: a graft copolymer of PLA and CS; a molecular chain-extended PLA; and crosslinked CS itself. These reactions resulted in the loss of hydroxyl groups. As a result, the

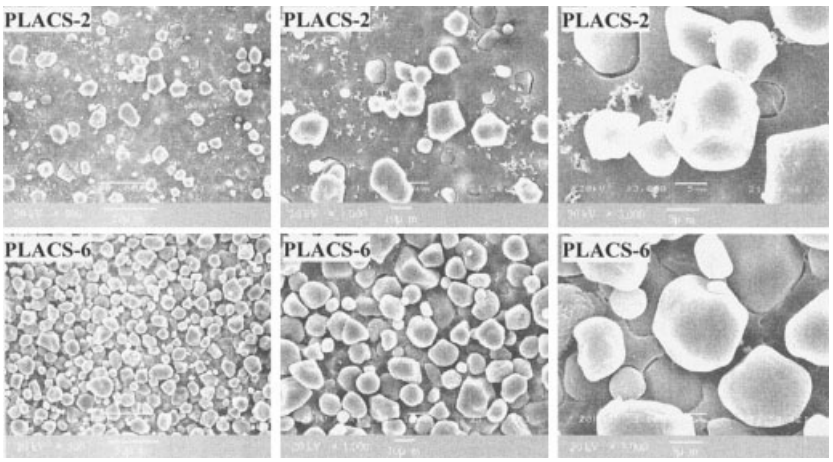

Figure 8 SEM micrographs of pure PLA and PLA/CS composite without LDI after enzymatic degradation. Sample code: PLACS2 (8 days) and PLACS6 (5 days).

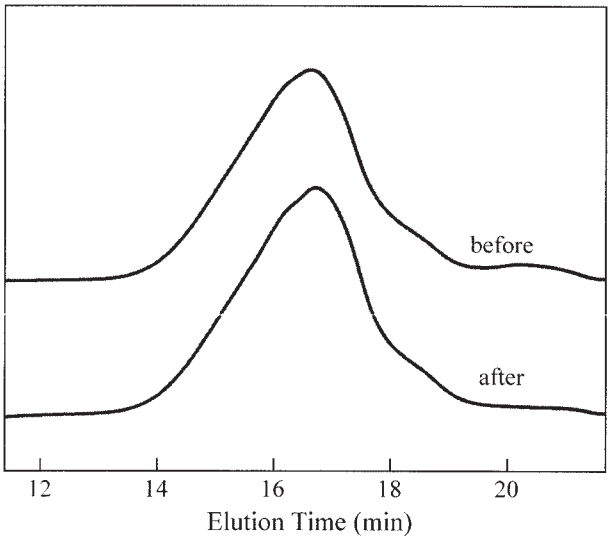

Figure 9 Molecular weight distribution of pure PLA before and after enzymatic degradation.

accessibility of the enzymes would be reduced. Flaqué et al. and Moreno-Chulim et al. reported that the graft reaction of vinylic and acrylic chains onto the OH groups of cellulose and starch reduced the accessibility of the enzymes produced by the microorganism, resulting in less biodegradation of grafted materials.[30,31]

Figure 6 shows the appearance after the enzymatic degradation. Clearly, all samples became reduced as enzymatic degradation proceeded. Figure 7 shows the SEM micrographs of pure PLA and PLA/CS (90/10 and 50/50) composites without LDI after enzymatic degradation. It can be seen that the degradation of pure PLA begins at the surface and the sheet becomes thin as the degradation proceeds. In the case of the composites without LDI, however, the degradation was faster at the interface between PLA and CS, with a deep and wide clearance created by the enzymatic degradation. As mentioned earlier, this may be due to the increased surface area exposed to the enzyme because of poor interfacial adhesion.

In the case of the composites with LDI, degradation at the interface between PLA and CS was not clearly observed, as shown in Figure 8. This may be due to the improved interfacial adhesion. That is, the improved interfacial adhesion would hinder the enzymes from accessing the interface between PLA and CS, and this would result in a longer degradation time.

Figure 9 shows the molecular weight distribution curves of pure PLA before and after enzymatic degradation. The molecular weights of all samples are summarized in Table III. Even though the weight remaining of all samples was drastically decreased by the degradation, the molecular weight and its distribution remained unchanged before and after enzymatic degradation. Iwata and Doi reported the same observations on the enzymatic degradation of PLA using Proteinase K.[14] These results imply that the degradation by Proteinase K would be surface erosion rather than nonspecific inner degradation, because the molecular weight was not changed by enzymatic degradation.

TABLE III
Molecular Weight and Polydispersity of Pure PLA and the PLA/CS (50/50) composites with and without LDI before and after Enzymatic Degradation for 2 Days

Sample code	Before degradation		After degradation	
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$
PLA	2.31	6.28	2.15	5.38
PLACS-5	1.90	4.78	1.88	4.88
PLACS-6	2.07	5.77	2.14	5.48

Figure 10 shows the yield of LA in a water-soluble product, which was obtained after the enzymatic degradation, as a function of the degradation time. In pure PLA and the PLA/CS (50/50) composite without LDI, the yield of LA increased drastically early in the degradation and then leveled off. It is of note that the increase in LA content was greater in the composite without LDI than in pure PLA. This may be due to the increased surface area of the PLA matrix in the composite due to poor interfacial adhesion with CS. On the other hand, the LA content of the composite with LDI gradually increased with degradation time and the values were the lowest for any sample. This result may be explained by the coupling effect of LDI. The terminal hydroxyl or carboxyl groups of PLA would be capped with LDI, resulting in a lowering of LA content.

Degradation in soil

It is well known that the degradation of PLA is very slow in soil. On the other hand, CS is easily biode-

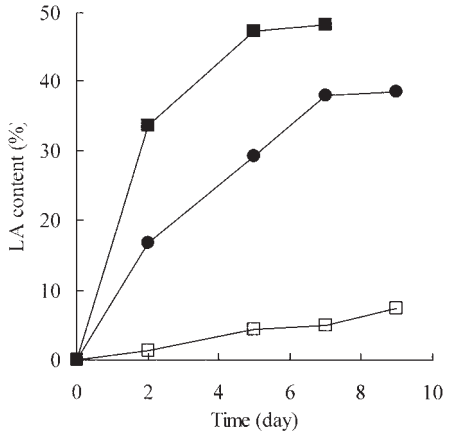

Figure 10 Dependency of LA content in water-soluble product of pure PLA and PLA/CS (50/50) composites with enzymatic degradation time; PLA (●), PLACS-5 (■), PLACS-6 (□).

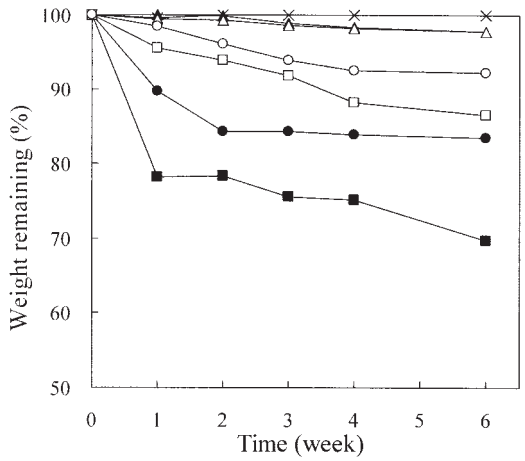

Figure 11 Weight remaining for pure PLA and PLA/CS composites with and without LDI plotted as a function of degradation time in burial tests; PLA (×), PLACS1 (▲), PLASC2 (△), PLACS3 (●), PLACS4 (○), PLACS5 (■), PLACS6 (□).

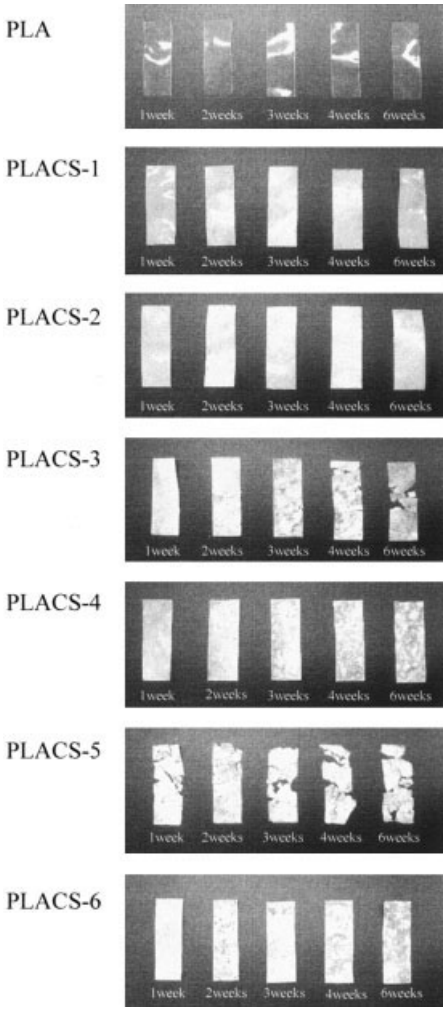

Figure 12 Photographs of pure PLA and PLA/CS composites with and without LDI before and after burial tests for 6 weeks.

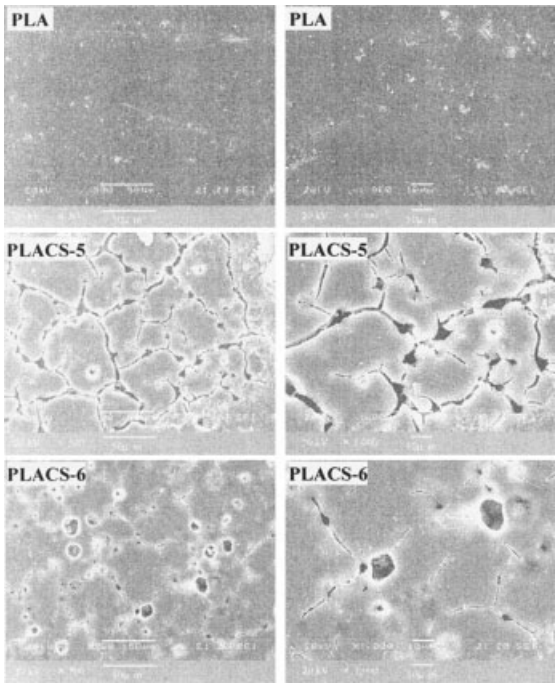

Figure 13 SEM micrographs of pure PLA and PLA/CS (50/50) composites with and without LDI after burial tests for 6 weeks.

graded by microorganisms such as fungi and bacteria in soil. So, the CS used as a filler in the composite would increase the degradation rate of the composite. The composite can be reduced into small particles causing minimal damage to the environment.

Figure 11 shows weight remaining for pure PLA and the PLA/CS composites with and without LDI as a function of degradation time. Except for pure PLA, which does not show any degradation, all composites were gradually degraded with time. With increasing CS content, the degradation rate increased. This is because CS is easily degraded in soil. When compared to the composite with LDI, the composite without LDI degraded easily, because poor interfacial adhesion between the PLA matrix and CS would increase the surface area of CS, and thereby, facilitate its degradation during exposure to microorganisms in soil.

Figures 12 and 13 show photographs and SEM micrographs of pure PLA and the PLA/CS (50/50) composite with and without LDI after 6 weeks of burial tests, respectively. It can be seen from Figure 12 that the PLA sheet remained unchanged, without any change in the original shape, whereas all the composites collapsed as degradation proceeded. However, there are differences in the degree of degradation between the composites with and without LDI. That is, the loss of shape occurred slower in the composites with LDI than without LDI. In the SEM micrographs shown in Figure 13, pure PLA did not show any degradation. In the composites, however, almost all

the starch particles on the surface of the composite were degraded, forming cracks and holes on the surface. These cracks and holes were produced by the degradation of CS. There were more cracks and holes in the composite without LDI than in the composite with LDI.

CONCLUSIONS

Thermal stability was decreased by addition of CS, and the composites with LDI showed higher thermal degradation temperature than those without LDI. From the results of enzymatic degradation using Proteinase K, it was found that PLA in the composite without LDI is easily degraded at the interface between CS and the PLA matrix. Thus, the improved interfacial adhesion due to the coupling effect of LDI made it difficult to degrade the PLA. In the case of burial tests, the degradation of the composite without LDI was easier than that of the composite with LDI. In conclusion, biodegradability could be adjusted by controlling the degree of interfacial adhesion, using LDI as a coupling agent.

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