Polyblend CPP and Bionolle with PP-*g*-MAH as Compatibilizer. II. Biodegradability

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ABSTRACT: The biodegradability of Bionolle and a CPP/Bionolle blend in two biotic environments, that is, soil and a lipase-enzyme solution, were evaluated using the mechanical properties and weight-loss data. It was noted that upon soil burial the tensile strength and elongation at break of polyblends were significantly reduced, particularly after 3 months. The time of complete loss of strength as predicted from the curve-fit model was found sequentially to be 6.80, 5.03, 4.84, 11.49, and 140.25 months for Bionolle, compatibilized Bionolle, and CPP/Bionolle (25/75), (50/50), and (75/25), respectively. Meanwhile, the weight loss of polyblends during soil burial were observed to generally increase with increasing Bionolle content. Even a synergistic effect on the weight loss was shown by compatibilized Bionolle and CPP/Bionolle (25/75). Additionally, the time for complete weight loss as estimated from the curve-fit model was 12.57, 7.33, 7.01, and 13.90 months for Bionolle, compatibilized Bionolle, and CPP/Bionolle (25/75) and (50/50), respectively. From the enzymatic degradation, it was recognized that in the early stage of biodegradation both the amorphous phase and the crystalline parts were randomly attacked. It was found that the weight loss that resulted from enzymatic degradation was satisfactorily described by a generalized kinetic curve derived from a first-order reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1283–1290, 1999

Key words: biodegradability; weight loss; synergistic effect; generalized kinetics

INTRODUCTION

The large number of synthetic polymers (plastics) being used around the world are relatively resistant to environmental degradation (photodegradation, hydrolysis, oxidation, biodegradation, and so forth). As a result, the used plastics may have a lifetime of hundreds of years, and this definitely becomes a serious problem in solid-waste management. In the literature,[1–6] various approaches have been considered to alleviate the harmful impact of plastic materials on the environment by designing and manufacturing biodegradable polymers. In general, the approach can be divided into three categories: The first is the incorporation of the chromophore or group susceptible to hydrolysis attack by microorganisms during the formulation. Polyester, polyamides, polyurethane, polyanhydride, and polyacetals are among examples of this polymer. The second is the development of naturally occurring processable bacterial polymer, for instance, polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and poly(hydroxyal-

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kanoic acid) (PHA). The third is the blending of a nonbiodegradable polymer and a biodegradable polymer.

Polypropylene (PP) is probably the second largest of plastic materials consumed in various fields in the world. From the literature,[7] it is known that PP has long been involved in the polyblend but that it was mainly blended with nonbiodegradable polymers. Up to recently, there have been only a few works that dealt with blending PP and biodegradable polymers.[8,9] Therefore, as reported in the previous article,[10] we attempted to blend CPP and Bionolle with Modic as a compatibilizer. It was shown that an almost compatible blend over a wide composition range can be obtained by the addition of 15 wt % Modic.

The current article was aimed at studying the biodegradability of a CPP/Bionolle blend. For this purpose, a biodegradation test was performed under two biotic environments, that is, a soil burial experiment and enzymatic degradation. The changes in the mechanical properties and the weight loss of the polyblend after being exposed to microbial attack or enzyme degradation were used as a measure of the biodegradability.

EXPERIMENTAL

Materials

CPP, Bionolle, and Modic as well as the blend preparation method used in this experiment were the same as previously mentioned,[10] unless otherwise stated.

Soil Burial Test

The standard-size dumbbell-shaped samples were buried in a soil mixture consisting of $\frac{1}{3}$ fermented leaves, $\frac{1}{3}$ pond soil, and $\frac{1}{3}$ garden soil. The biodegradation test was performed in the laboratory but the soil temperature was not controlled and fluctuated from about 5 to 27°C (during winter and summer seasons). The moisture content of the soil was maintained about 30%, and the pH, around 6. The samples were removed after 1, 3, 5, and 7 months and washed thoroughly with water and dried at room temperature and subsequently in a vacuum oven at about 50°C for at least 24 h. The weight loss was calculated using the following equation:

$$\text{Weight loss } (\%) = (W_0 - W_{\text{soil}})/W_0 \times 100$$

W_0 and W_{soil} are the weight of the sample before and after soil burial, respectively.

Enzymatic Degradation

Because the enzyme assay is very specific in nature, it is important to determine first the optimum conditions for the occurrence of an enzymatic reaction. In this respect, the method for enzymatic degradation was proposed by us since the available method did not result in any significant degradation. The method was developed on the basis of the method proposed by Tokiwa and Komatsu,[11] Standler et al.,[12] and Iwamoto and Tokiwa.[8] In principle, the system consists of a mixture of three aqueous solutions:

- Phosphate buffer solution (ca. 0.2*M*).
- Lipase AK-enzyme solution at different concentrations.
- Potassium hydroxide solution (0.01*N*).

The pH of the solution was adjusted to about 7.1

Bionolle film, 10–20 mg, with a size of about 1 $\times$ 1 cm^2 and thickness of 0.1 mm was put into a reaction tube which contained 6 mL of the mixture solutions. The reaction was performed at different temperatures (25–80°C) and duration times (12 h to 6 days). After reaction, the sample was removed and washed with water and dried at room temperature and, subsequently, using a vacuum oven (ca. 50°C) to a constant weight. The weight loss due to enzymatic degradation was calculated using the following equation:

$$\text{Weight loss } (\%) = (W_0 - W_{\text{enzyme}})/W_0 \times 100$$

W_0 and W_{enzyme} denote the weight of the sample before and after enzymatic degradation, respectively.

RESULTS AND DISCUSSION

To evaluate the biodegradability of polymers and polyblends after being subjected to microbial attack (soil burial), the mechanical properties were monitored and are presented in Figure 1(a,b). As shown in these figures, it was observed that the tensile strength and elongation at break of Bionolle, compatibilized Bionolle, and CPP/Bionolle (25/75) decreased steeply along with the burial time, whereas with compatibilized CPP/Bionolle

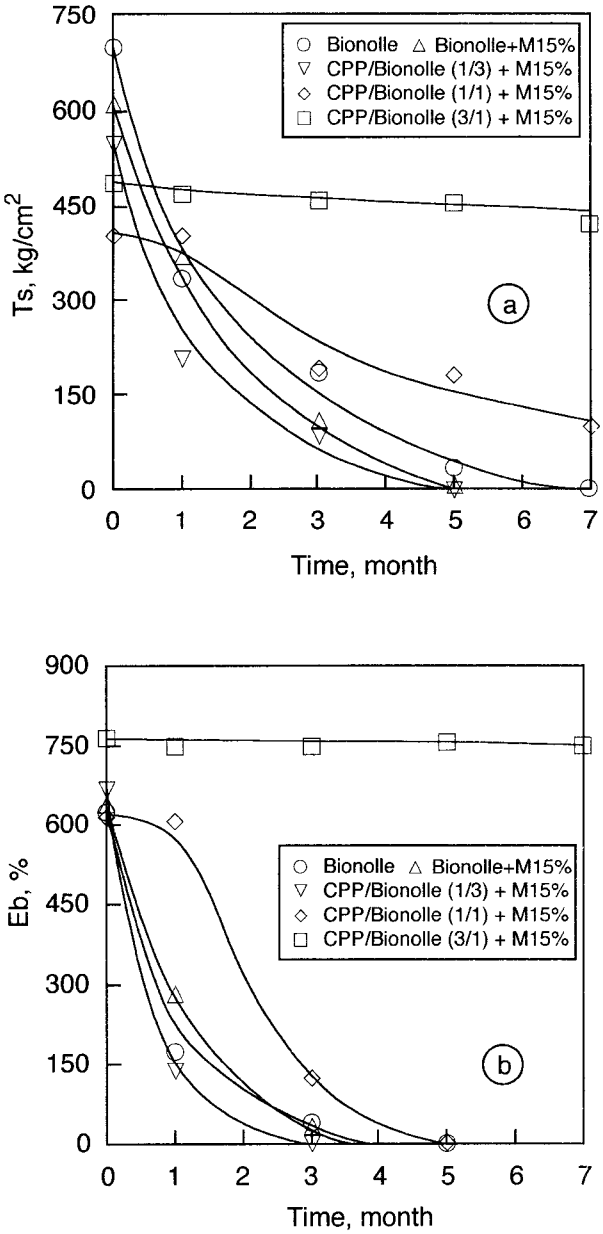

Figure 1 Changes in the tensile strength (T_s) and elongation at break (E_b) of Bionolle, compatibilized Bionolle, and CPP/Bionolle blends during soil burial.

(50/50), a sharp decrease occurred after 1 month. It was surprisingly noted that the compatibilized Bionolle and CPP/Bionolle (25/75) samples showed a lower tensile and elongation than did Bionolle itself, indicating that their biodegradability was higher. This unusual case was probably due to a synergistic effect that arose from Bionolle and Modic as a compatibilizer. Bionolle, by its nature, is liable to microbial attack, causing a drastic reduction in the mechanical properties, while Modic dispersed the minor phase of CPP to significantly finer droplets and embedded it in the continuous phase of Bionolle, leading to the formation of a so-called cocontinuous phase (see SEM micrograph in Fig. 2d in ref. 10). In this morphology, the microbes seem to randomly attack and penetrate the blend as a whole matrix. Thus, the sharp increase of the loss strength constant (K, see Fig. 4) was observed at 50–75 wt % Bionolle. In contrast, as the fraction of Bionolle was decreased to 50 and 25 wt %, the phase morphology progressively changed from the dispersed phase of CPP to the dispersed phase of Bionolle (Fig. 2e,f in ref. 10). If the biodegradable polymer, that is, Bionolle, is dispersed within a nonbiodegradable matrix, that is, CPP, Bionolle is protected from microbial attacks and from degradation by the surrounding layer of CPP. As a result, the biodegradability of the polyblend will certainly decrease or, in other words, the mechanical properties will remain high, whereas the compatibilized CPP and pure CPP were almost unaffected (see Fig. 2). A similar case was also reported by Iwamoto and Tokiwa,[8] in which PCL in the PCL/PP blend was not readily degraded by the enzyme when PCL was presented as a dispersed phase.

To estimate when the complete loss of strength is reached, an attempt was made to find a correlation model that can best fit the relation between tensile strength and soil burial time. It was noted that if the square root of the relative tensile strength, $(T_s/T_{s,0})^{1/2}$ ($T_{s,0}$ and T_s denote the ten-

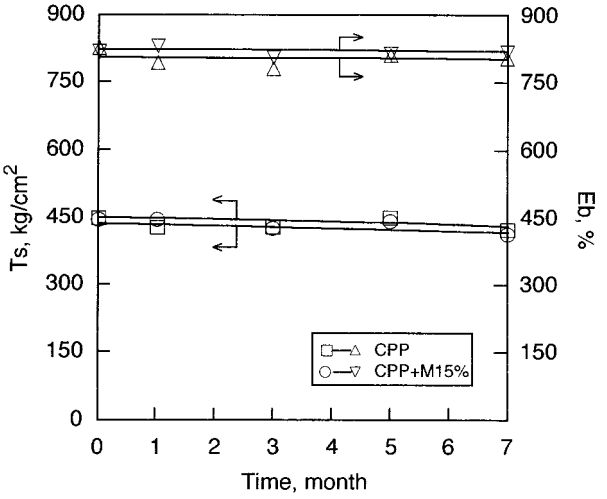

Figure 2 Changes in the tensile strength (T_s) and elongation at break (E_b) of CPP without and with the compatibilizer during soil burial.

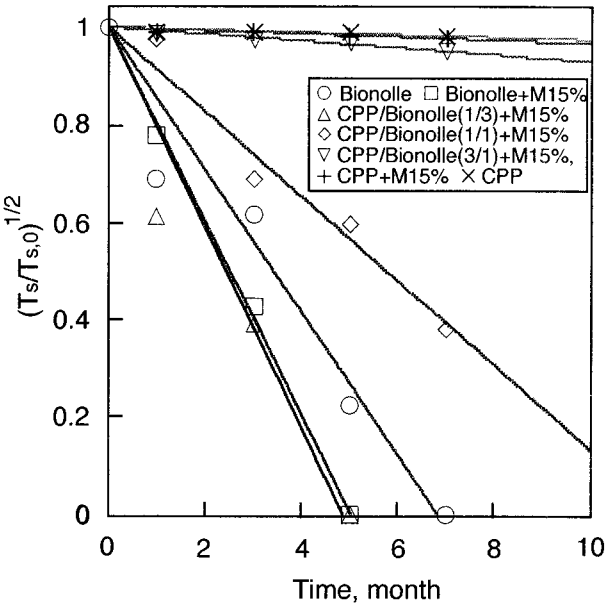

Figure 3 Dependence of the relative tensile strength ($T_s/T_{s,0}$) for uncompatibilized and compatibilized CPP and Bionolle and the CPP/Bionolle blend on the soil burial time.

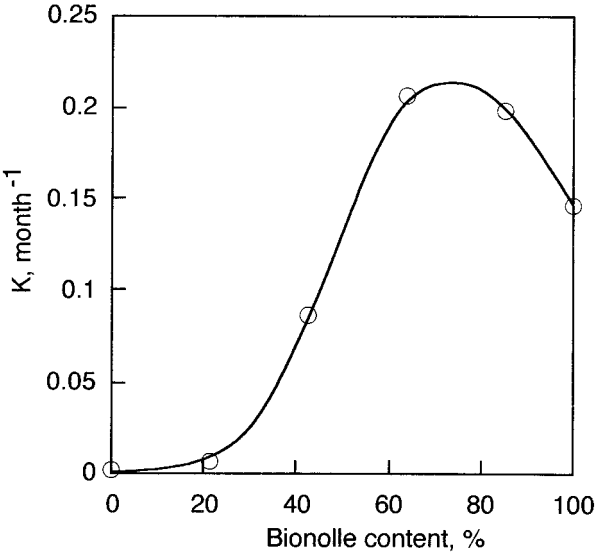

Figure 4 Dependence of the loss of strength rate constant (K) on the Bionolle content for the compatibilized CPP/Bionolle blend buried in soil.

sile strength of the sample before and after soil burial, respectively) is plotted against burial time (see Fig. 3) the linear model was the best one to describe the relation with a coefficient of determination, r^2, approaching 1. Using this model, the time of complete loss of strength was calculated. It was sequentially found to be 6.80, 5.03, 4.84, 11.49, and 140.25 months for Bionolle, compatibilized Bionolle, and CPP/Bionolle (25/75), (50/50), and (75/25), respectively. In addition, the plot of the loss strength rate constant (K = slope of the Fig. 3) versus the Bionolle content (shown in Fig. 4) clearly reflects that the rate of biodegradation increased with an increasing Bionolle fraction in the ternary blends. The maximum value of K was achieved at about 70% of the Bionolle fraction (CPP/Bionolle: 15/85).

To obtain a quantitative idea about the biodegradability of polymers and polyblends, the weight loss after soil burial was measured and is given in Figure 5. It is obvious that the CPP/Bionolle (25/75) blend shows the highest rate of weight loss, subsequently followed by compatibilized Bionolle, Bionolle, and CPP/Bionolle (50/50). These results certainly support the previous explanation of the synergistic effect on the mechanical properties which bring about a lower tensile strength and elongation at break. Furthermore, with the aid of a computer, the best curve-fit model that can describe the kinetics of weight loss has been determined as a parabolic model. From this model, it is possible to predict when the complete biodegradation or weight loss of 100% can be

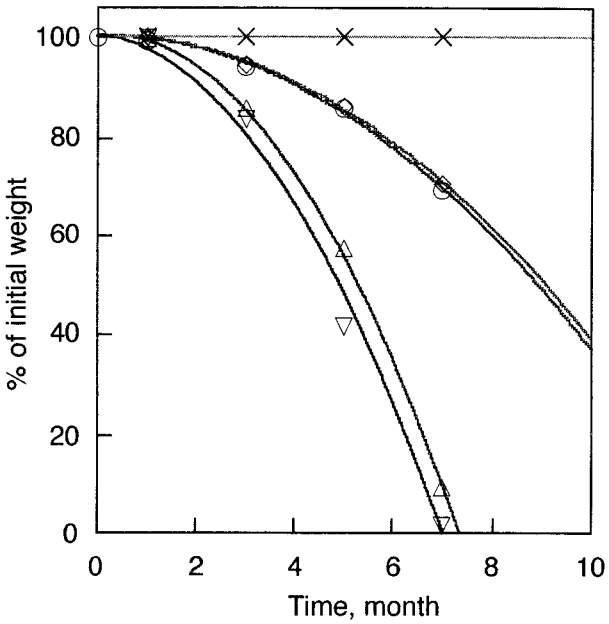

Figure 5 Macrokinetics of the weight loss for the sample buried in soil: (○) Bionolle; (△) Bionolle + M15%; (▽) CPP/Bionolle (1/3) + M15%; (◇) CPP/Bionolle (1/1) + M15%; (×) CPP/Bionolle (3/1) + M15%, CPP + M15%, and CPP.

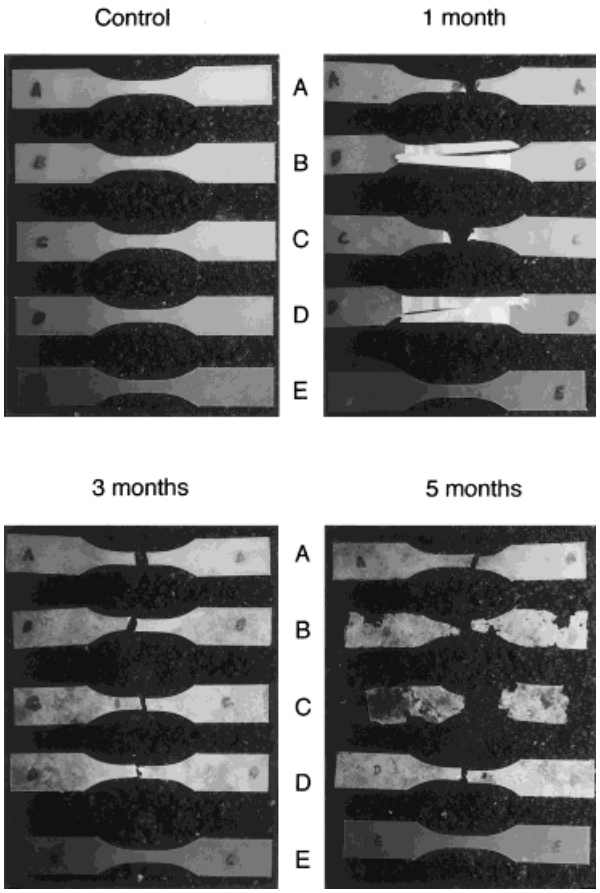

Figure 6 Photographs of the samples before and after biodegradation in soil for 1, 3, and 5 months: (A) Bionolle; (B) Bionolle + M15%; (C) CPP/Bionolle (1/3) + M15%; (D) CPP/Bionolle (1/1) + M15%; (E) CPP/Bionolle (3/1) + M15%.

achieved, which was found to be 12.57, 7.33, 7.01, and 12.75 months for Bionolle, compatibilized Bionolle, CPP/Bionolle (25/75), and (50/50), respectively. From Figure 5, one can also observe that the role of Bionolle as the main carbon source for the microbes diminishes when it presents in the blend sample containing rich CPP. Again, because at a higher content of CPP (CPP/Bionolle (75/25) or higher), in addition to Bionolle in a dispersed phase, it was mostly covered by CPP. As a result, Bionolle was not efficiently attacked or removed from the blends. Therefore, it is not surprising when there was no weight loss recorded in the polyblend containing minute Bionolle, and, of course, the compatibilized CPP and pure CPP would not give any weight loss.

To visualize the course of biodegradation during soil burial, a photograph of the sample was taken and is presented in Figure 6. Compared with the control sample, a significant change in physical appearance is clearly seen. Without any difficulties, particularly after 3 months, one can easily distinguish which sample has undergone more biodegradation. For example, compatibilized CPP/Bionolle (25/75) was noted to suffer much more microbial attack, since its physical performance was severely deteriorated. On the contrary, the compatibilized CPP/Bionolle (75/25) blend was observed to remain almost unchanged, indicating that its biodegradability was very low.

To investigate in more detail the course of biodegradation, the enzymatic test is probably the most convenient way to model the biodegradation. It allows one to perform biodegradation in a relatively very short time (in the order of hour or day) and to simplify the complex reactions of living processes. As shown in Figure 7, under control biodegradation conditions, the weight loss of Bionolle up to 6 days of reaction time has been monitored. It was observed that the weight loss increased with increasing reaction time until the equilibrium state was reached. The maximum weight loss was achieved within 6 days and was between 7 to 45 wt %, depending on the enzyme concentration. It appears that 0.2% of the lipase enzyme was the optimum (see Fig. 8). Beside that, the role of the hydrolytic process on the biodegradation was observed to be negligible since no significant weight loss resulted from the enzyme-

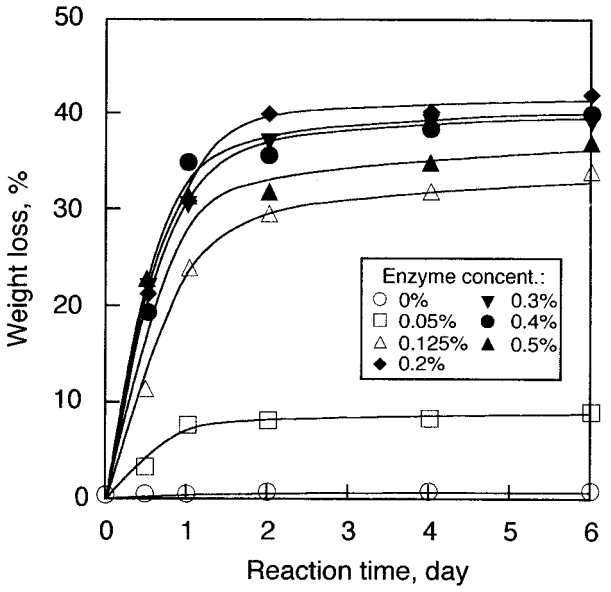

Figure 7 Weight loss of Bionolle during enzymatic reaction at different concentrations of lipase AK–enzyme. Reaction temperature: 70°C.

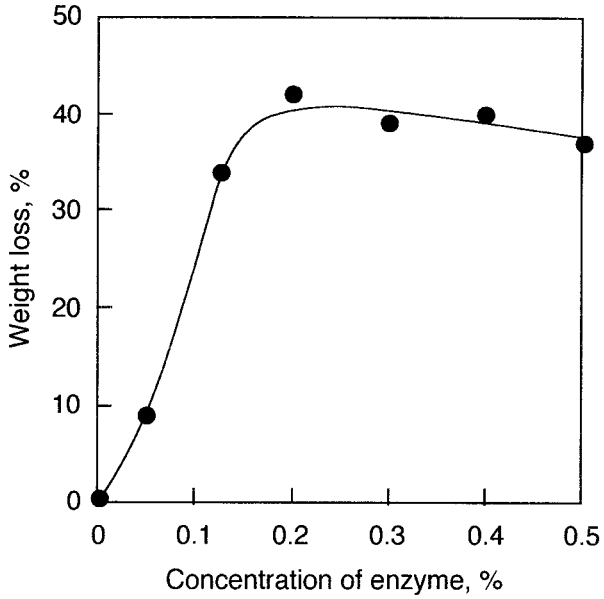

Figure 8 Effect of enzyme concentration on the weight loss of Bionolle. Reaction time: 6 days; reaction temperature: 70°C.

free solution. Additionally, interestingly, all the weight loss kinetics correlate very well with a single generalized kinetic curve (Fig. 9) that originally was derived from a first-order reaction in dimensionless ordinates:

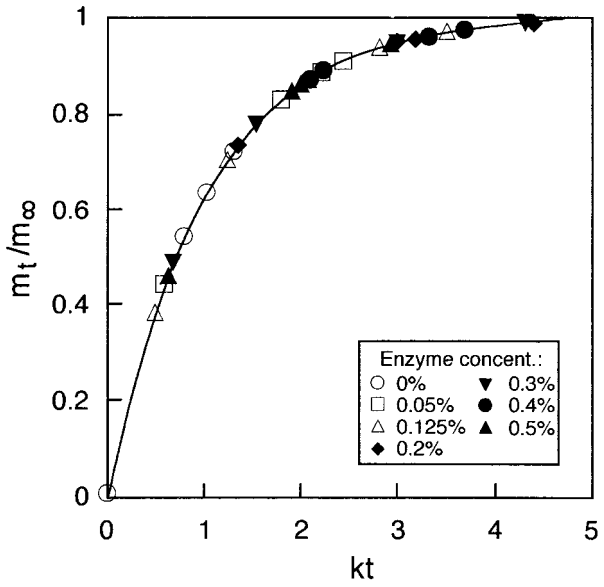

Figure 9 Generalized kinetic curve of the weight loss for enzymatic degradation of Bionolle (using data of Fig. 7).

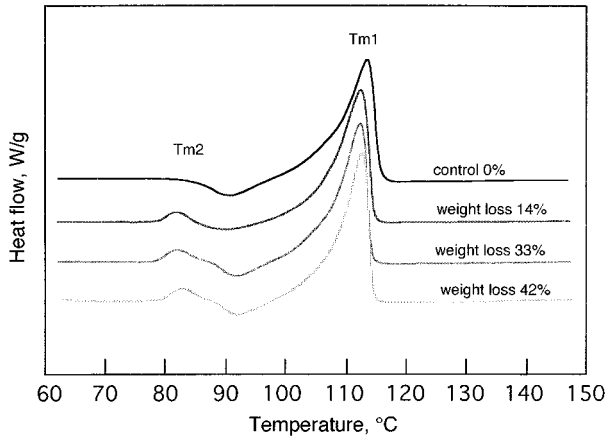

Figure 10 DSC thermogram of Bionolle before and after enzymatic degradation at 70°C and 0.2% enzyme concentration.

$$M_t/M_\infty = 1 - \exp(-kt)$$

where M_t is the weight loss at time t (mg); M_∞, the weight loss at the equilibrium state (mg); k, the time-dependent rate constant (1/day); and t, the reaction time (day).

The DSC data presented in Figure 10 and Table I may be accounted for by the mechanisms of the biodegradation. In a semicrystalline polymer like Bionolle, there is a commonly accepted fact that microorganisms or enzymes preferably attack the amorphous phase, leaving a residual porous predominantly crystalline part.[13–16] In fact, the observed crystallinity as reflected by the heat of fusion at the early stage of enzymatic degradation was not increased and even was decreased. This implies that the crystalline part was simultaneously destroyed or broken into a small fragment, and a small additional melting peak appearing at about 82°C was evidence. In the course of time, however, an increase in the overall crystallinity was brought about (as the heat of fusion of the small and main peaks gradually increased). Obviously, this indicates that while the preferential degradation proceeded in the amorphous phase further degradation also occurred in the crystal parts, as well as in the main crystals but at a slower rate.[17] This process is presumed to take place repeatedly until complete degradation is achieved. Additionally, the annealing effect in the course of degradation was not taken into consideration since the temperature reaction (70°C) is still far below the melting temperature of Bionolle (ca. 113°C). From Figure 11, the effect of the reaction temperature on the weight loss is

Table I Changes in the Crystallinity as Reflected by the Changes in the Heat of Fusion of Bionolle After Enzymatic Degradation at 70°C and 0.2% of Enzyme Concentration

	Main Peak		Small Peak	
Weight Loss (%)	T_{m1} (°C)	H_f (J/g)	T_{m2} (°C)	H_f (J/g)
0	112.9	78.8	—	—
14	111.8	73.9	80.6	4.6
33	111.7	76.7	81.0	9.6
42	112.1	78.4	81.8	9.4

straightforward. It is apparent that as the reaction temperature increased the weight loss also increased up to maximum and, thereafter, dropped steeply. This is a well-known effect. At a reasonably high temperature, the enzyme undergoes denaturation, and, accordingly, it will lose reactivity. On the other hand, at a relatively low temperature, the enzyme is not reactive enough.

CONCLUSIONS

It has been demonstrated that incorporation of a biodegradable polymer into a blend system enables the manufacture of biodegradable polyblends. The characteristic of the biodegradability of a polyblend was that it was composition-dependent. For example, in the case of the blend composition of CPP/Bionolle (25/75), the highest value of weight loss was observed. On the other hand, zero weight loss was noticed if the blend composition was 75/25. The higher value of the weight loss in compatibilized Bionolle and CPP/Bionolle (25/75) blends compared to pure Bionolle was due to a synergistic effect.

From the enzymatic experiments, it is inferred that in the early stage of biodegradation enzyme attacks heterogeneously both the amorphous phase and the crystalline region. However, in the course of time, as expected, biodegradation occurs preferentially in the amorphous phase and in a small crystal part. Additionally, it was found the all the weight loss can be satisfactorily described by a single generalized kinetic curve.

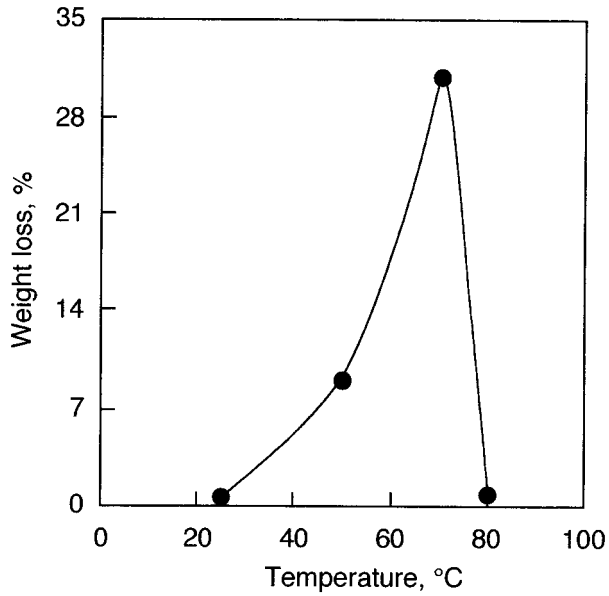

Figure 11 Effect of temperature on enzymatic degradation of Bionolle. Enzyme concentration: 0.2%; reaction time: 1 day.

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