

Biodegradation of Poly(butylene adipate-co-butylene terephthalate)/Layered-Silicate Nanocomposites

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ABSTRACT: The biodegradability of poly(butylene adipate-co-butylene terephthalate) (PBAT) and PBAT/starch composites with layered silicates prepared by melt intercalation was evaluated with aerobic biodegradability tests in soil and in an aqueous medium containing activated sludge. Nonmodified montmorillonite (MMT) and octadecylamine-modified montmorillonite (ODA-M), known to give a microcomposite and an intercalated nanocomposite for PBAT, respectively, were used as layered silicates. After they were buried in the soil for 8 months, the PBAT/MMT microcomposite exhibited a higher

weight loss than the control PBAT, whereas the PBAT/ODA-M nanocomposite showed a lower weight loss instead. Also, the biodegradability test in the aqueous medium, by determining the biochemical oxygen demand, showed that the addition of MMT and/or starch to PBAT promoted biodegradation, whereas the addition of ODA-M did not. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 730–736, 2007

Key words: biodegradable; degradation; nanocomposites; organoclay; polyesters

INTRODUCTION

Nanocomposites based on biodegradable polyesters and layered silicates have been attracting attention because layered clay is environmentally friendly, naturally abundant, and economic, and the improvement of various properties in comparison with control biodegradable polymers can enlarge the application fields of the polymers. The morphologies and physical properties of nanocomposites of biodegradable polyesters such as poly(lactic acid),^{1–5} poly(ϵ -caprolactone),^{6–9} poly(hydroxybutyrate-co-valerate),^{10,11} poly(butylene succinate) (PBS),^{12–14} and poly(butylene adipate-co-butylene terephthalate) (PBAT)¹⁵ have been already studied by several groups. However, few publications have reported on the biodegradability of these nanocomposites.^{7,11} Regarding the biodegradability of nanocomposites containing PBS-related polymers, Lee et al.¹⁶ reported that a nanocomposite of an aliphatic polyester derived from aliphatic glycols (ethylene glycol and 1,4-butanediol) and aliphatic dicarboxylic acids (succinic acid and adipic acid) showed lower biodegradability than the control polymer when the samples were buried in activated soil for 30 days.¹⁶ To the best of our knowledge, no study regarding the biodegradability of PBAT-related nanocomposites has been published so far. In our previous article,¹⁵ we investigated the morphologies and mechanical and thermal properties of PBAT composites with unmodified montmorillonite

(MMT) and various organomodified MMTs. Microscale clusters of MMT were observed in PBAT/MMT composite samples, and an intercalated nanocomposite was formed in the case of a PBAT/octadecylamine-modified montmorillonite (ODA-M) composite with an inorganic concentration of 5–10 wt %. In this article, the biodegradability of PBAT/MMT and PBAT/ODA-M composite films is investigated in detail through aerobic biodegradability tests in soil and in an aqueous medium with activated sludge. Because the biodegradability of PBAT itself is not so high, the addition of highly biodegradable starch to the PBAT composites is also investigated.

EXPERIMENTAL

Materials

PBAT [Ecoflex; melt flow rate at 190°C and 2.16 kg = 3.3–6.6 g/10 min, specific gravity = 1.26, glass-transition temperature = –30°C (differential scanning calorimetry), melting temperature = 115°C (differential scanning calorimetry), butylene terephthalate/adipate composition \approx 4/6] was supplied by BASF Japan, Ltd. (Tokyo, Japan). Sodium MMT (Kunipia F; cation-exchange capacity = 115 mequiv/100 g) was supplied by Kunimine Industries Co., Ltd. (Tokyo, Japan). Octadecylamine (ODA) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). The starch used in this study was a high-amylose corn starch (Japan Maize Products Co., Ltd., Tokyo, Japan). It contained 70% amylose and 30% amylopectin. All the other chemicals used in this work were reagent-grade and were used without further purification.

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The MMT modified with ODA was prepared with the same procedure reported in the literature.^{13,14} All the other chemicals used in this work were reagent-grade and were used without further purification.

Preparation of the PBAT composite samples

MMT and ODA-M were dried *in vacuo* at 40°C for at least 24 h before use. The melt mixing of PBAT, starch, and clay particles was performed on a Laboplasto-Mill with a twin-rotary roller mixer (Toyo Seiki Co., Ltd., Tokyo, Japan). The starch and inorganic concentrations of the composites were 0, 10, and 20 wt % and 0, 5, and 10 wt %, respectively. The PBAT/starch/ODA-M composite with a starch concentration of 10 wt % and an inorganic concentration of 5 wt % (85 : 10 : 6.8 w/w/w) was abbreviated PBAT/starch10/ODA-M5. The mixing was carried out for 5 min at a rotary speed of 50 rpm at 140°C. The mixture was crushed into small pieces after immersion in liquid nitrogen and dried at 40°C *in vacuo* for at least 24 h before the injection molding. The dumbbell-shaped specimen (5 mm wide, 2 mm thick, 32 mm long for the parallel part, and 72 mm long in all) was molded with a desk injection-molding machine (Little-Ace I type, Tsubako Co., Ltd., Chigasaki, Japan). The cylinder temperature and molding temperature during the injection molding were 200 and 60°C, respectively. Film specimens about 0.30 mm or 30 μm thick for weight-loss testing after soil burial and biochemical oxygen demand (BOD) testing in an aqueous medium, respectively, were prepared by the hot pressing of the dumbbell-shaped composites at 140°C and 10 MPa over 5 min. The obtained films were cut into 40 mm × 20 mm and 10 mm × 5 mm rectangular specimens for the weight-loss and BOD testing, respectively.

Measurements

Tensile tests of the composites were performed with an Autograph AG-I (Shimadzu Co., Ltd., Tokyo, Japan) according to the standard method for testing the tensile properties of plastics [JIS K7113 (1995)]. The span length was 50 mm, and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and standard deviation were calculated.

X-ray diffraction (XRD) analysis was performed at the ambient temperature on a Rigaku RINT-2100 X-ray diffractometer (Tokyo, Japan) at a scanning rate of 2.0°/min with Cu K α radiation (wavelength = 0.154 nm) at 40 kV and 14 mA. Sodium MMT and the freeze-dried organoclay were studied as powders. The film samples, 0.30 mm thick, were prepared for the XRD measurements in a manner similar to the preparation of the weight-loss samples.

The biodegradability was determined by the measurement of the weight loss of the composite films after they were buried in soil. The soil used in this test was a 1 : 1 mixture of black soil and leaf mold for gardening. Each specimen was buried in the soil in planters and incubated at room temperature (15–30°C). Water was supplied at intervals of 2 days, and the soil was kept not to be dried. Each specimen was dug out of the soil after it was buried for 30, 90, 150, 180, 210, and 240 days. The obtained specimens were washed with water and dried to a constant weight at 40°C in a vacuum oven. Two specimens were tested for each set of samples with the prescribed incubation time, and the mean value was calculated.

The biodegradability was also determined according to JIS K6950 by the measurement of BOD in an aerobic, aqueous medium containing activated sludge. To a phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl₂, 0.09 mM MgSO₄, 0.09 mM NH₄Cl, and 0.9 μM FeCl₃ was added 3.13 mL of the activated sludge containing 50 mg of the suspended part, which was obtained from sewage facilities of the Chiba Institute of Technology, and 20 mg of the film sample. The suspension was steadily stirred with a magnetic stirring bar. BOD was measured at 25°C with a Taitec 200F BOD tester (Koshigaya, Japan). Carbon dioxide was absorbed into a 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. The volume of the consumed oxygen was directly measured with a scaled cylinder. The biodegradation of the composites was calculated with the following equation:

$$\begin{aligned} \text{Biodegradation (\%)} &= [(\text{BOD of the sample at time } t \\ &\quad - \text{BOD of the blank at time } t) / \\ &\quad \text{Theoretical oxygen demand}] \times 100 \quad (1) \end{aligned}$$

The theoretical oxygen demand was calculated from the composition and structural formula of the PBAT copolymer and starch under the assumption that the degraded products were completely mineralized to CO₂. The degradation of the organic fraction of ODA-M was ignored in this calculation.

Optical pictures of the obtained specimens were taken with a digital camera (Camedia C-40 Zoom, Olympus, Tokyo, Japan). The morphology of the specimen surface was observed with a JSM-6300 scanning electron microscope (Japan Electron Co., Ltd., Tokyo, Japan). Before the observation, the specimens were coated with Au by the sputtering process to achieve optimal imaging.

RESULTS AND DISCUSSION

Characterization of the PBAT/starch composites

Figure 1 shows the XRD charts of the PBAT/clay and PBAT/starch/clay composites with inorganic concen-

trations of 5 and 10 wt %. All the PBAT/MMT and PBAT/starch/MMT composites showed XRD peaks at almost the same position as that of pure MMT, indicating that no intercalation occurred. There was little influence of the starch and MMT content on the inter-

layer spacing of the aluminosilicates in the composites. On the other hand, the XRD peaks of the PBAT/ODA-M and PBAT/starch/ODA-M composites ($2\theta = 2.6\text{--}3.1^\circ$, $d = 2.9\text{--}3.3$ nm) were considerably lower than that of pure ODA-M ($2\theta = 4.04^\circ$, $d = 2.19$ nm),

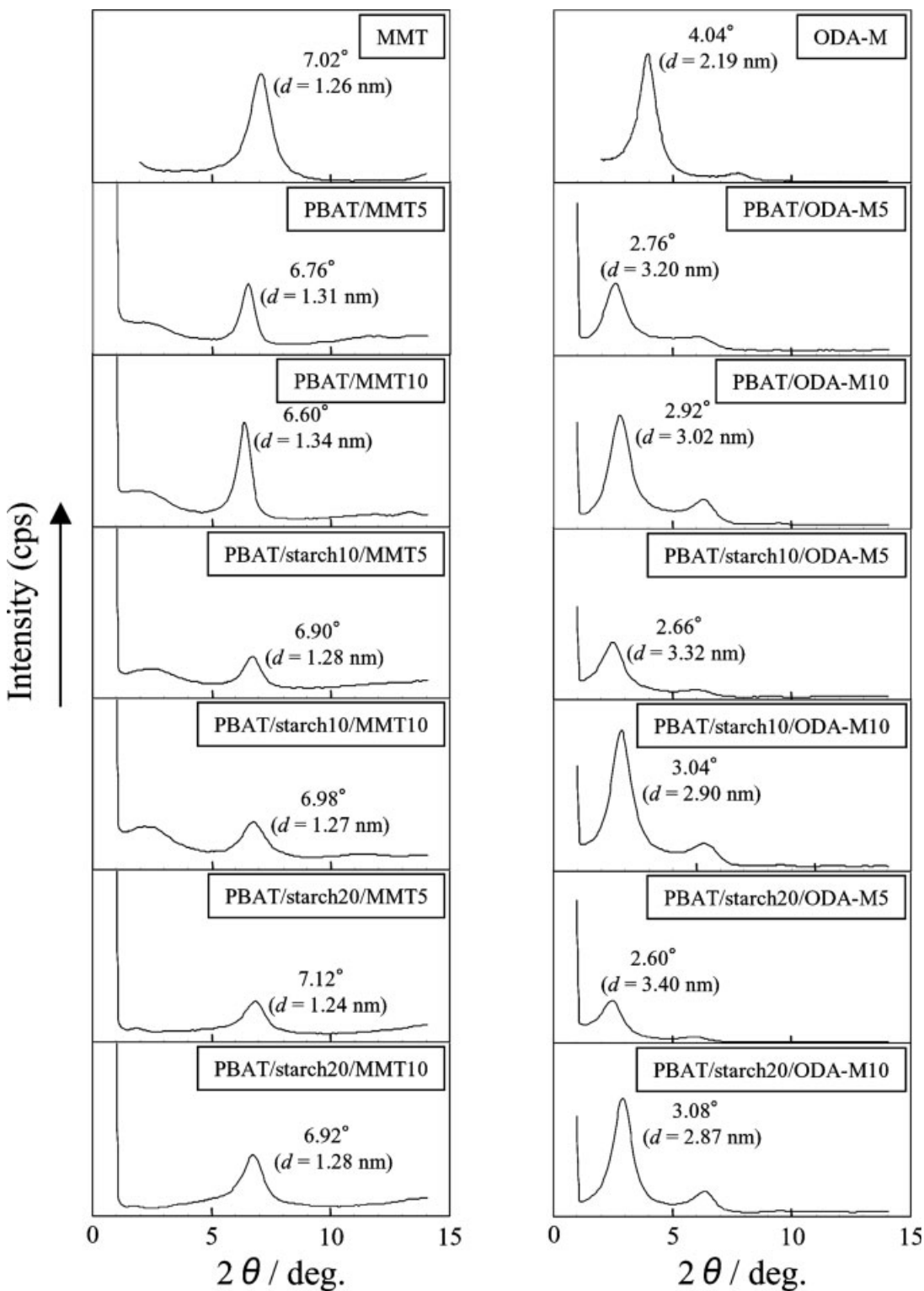


Figure 1 XRD patterns of clays, PBAT/clay, and PBAT/starch/clay.

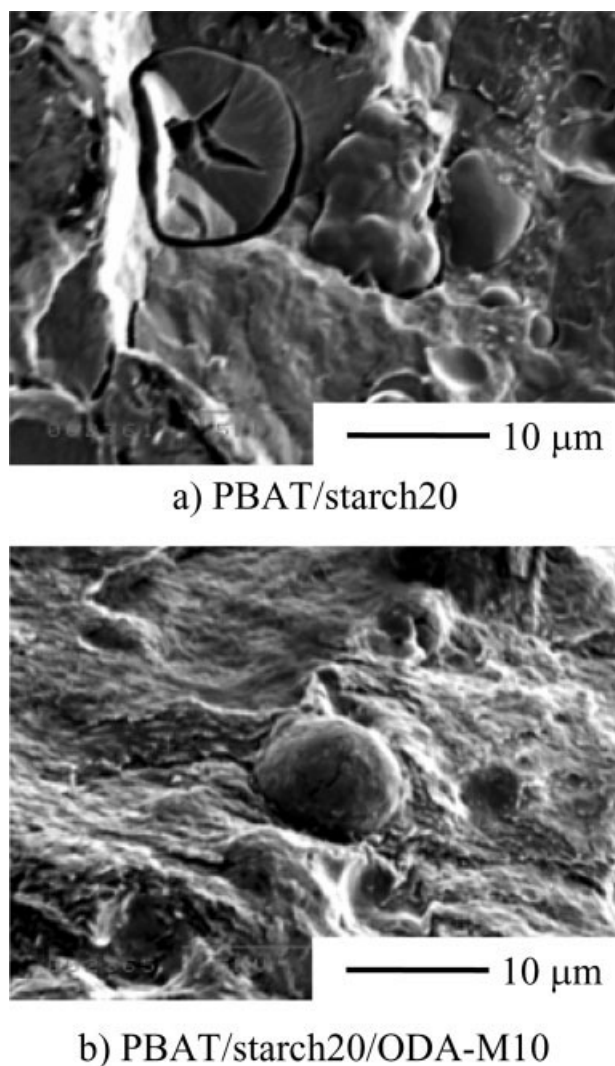


Figure 2 SEM micrographs of the fracture surfaces of (a) PBAT/starch20 and (b) PBAT/starch20/ODA-M10.

indicating that intercalated nanocomposites had formed. The ODA-M composites with an inorganic concentration of 10 wt % showed a lower interlayer spacing than the ODA-M composites with 5 wt %, indicating that the extent of intercalation became lower with increasing inorganic content. The influence of the starch content was also little for the ODA-M composites.

Figure 2 shows scanning electron microscopy (SEM) micrographs of the fracture surfaces of PBAT/starch20 and PBAT/starch20/ODA-M10. For both samples, starch particles (<10 μm) were dispersed in the PBAT matrix. The surface of the PBAT matrix for the latter composite appeared sandy because of the presence of ODA-M. Upon the melt mixing of PBAT/starch and ODA-M, it is thought that ODA-M was not present in the starch particles because the starch did not melt at 140°C.

We already reported that the addition of MMT or ODA-M to PBAT caused an increase in the modulus

and a slight decrease in the strength.¹⁴ Figure 3 shows the tensile properties of all the composites as a function of the starch content. On the whole, the addition of starch caused an increase in the tensile modulus and decreases in the tensile strength and elongation at break. The PBAT/starch/ODA-M composites showed higher tensile strength and modulus than the PBAT/starch/MMT composites in a trend similar to that of

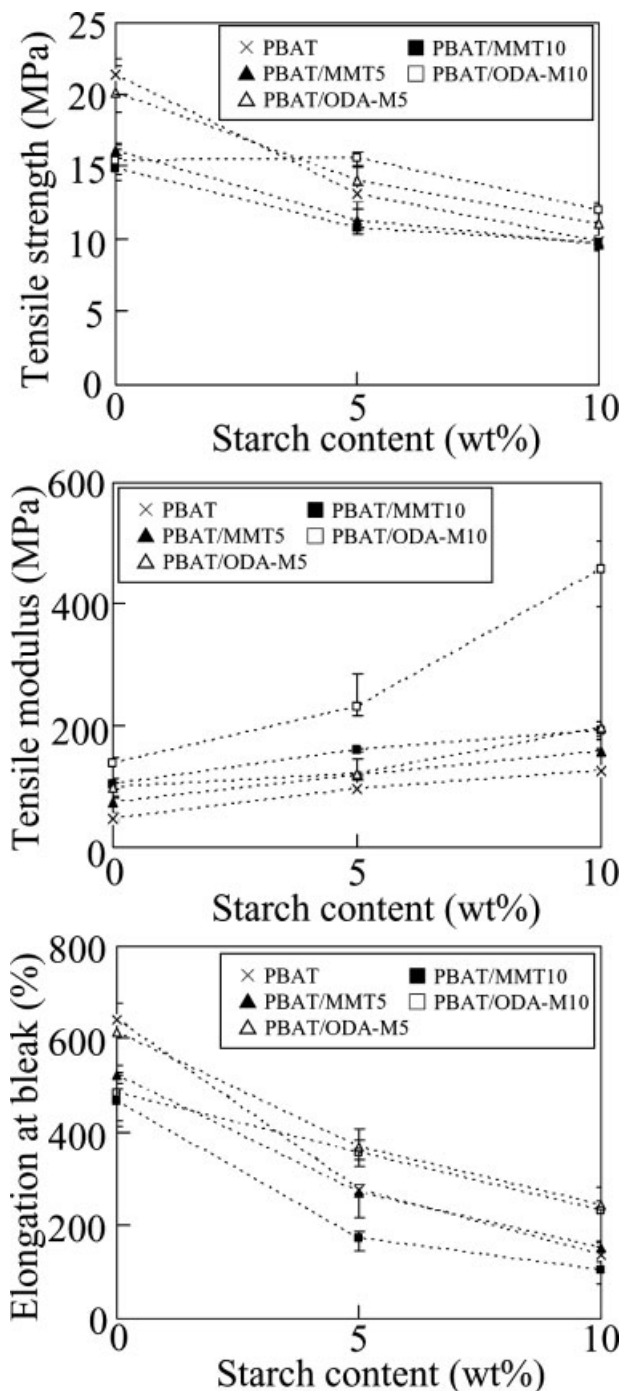


Figure 3 Tensile properties of PBAT composites as a function of the starch content.

the PBAT/ODA-M and PBAT/MMT composites without starch.

Biodegradability of the PBAT composites buried in the soil

Figure 4 shows the change in the weight loss of the control PBAT, PBAT/MMT, and PBAT/ODA-M during the burial in soil. The weight loss after 240 days for the PBAT/MMT10 composite was about 4%, which was the largest value of all the samples containing the control PBAT. On the other hand, that of the PBAT/ODA-M10 composite was about 1%, which was the lowest of all. Figures 5 and 6 show the weight loss of the composites containing 10 and 20 wt % starch, respectively. The weight loss of the composites containing 10 wt % starch was not so high in comparison with that of the corresponding composites without starch. It is thought that a little starch was present on the uppermost surface of the films containing 10 wt % starch. Among the composites containing 20 wt % starch, the PBAT/starch20/MMT10 composites showed the highest weight loss (ca. 8% at 240 days). However, as was obvious from the starch content of this composite, the starch component did not completely decompose even after 240 days, and this suggested that the starch coated with PBAT did not easily decompose. Also, for the PBAT composites containing starch, the MMT composites showed higher weight loss than the ODA-M composites. In this soil burial test, the weight loss was small on the whole, and some plots had a considerable error bar. Therefore, the trend deduced from the soil burial test was confirmed by the following surface observation and BOD test.

Figure 7 shows optical photographs of the surfaces of the samples buried in the soil for 240 days. Coloring and roughing were promoted by the addition of starch

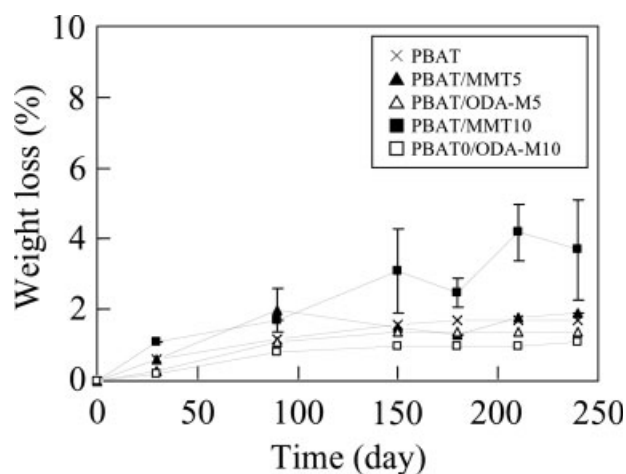


Figure 4 Weight loss of PBAT, PBAT/MMT, and PBAT/ODA-M after they were buried in soil.

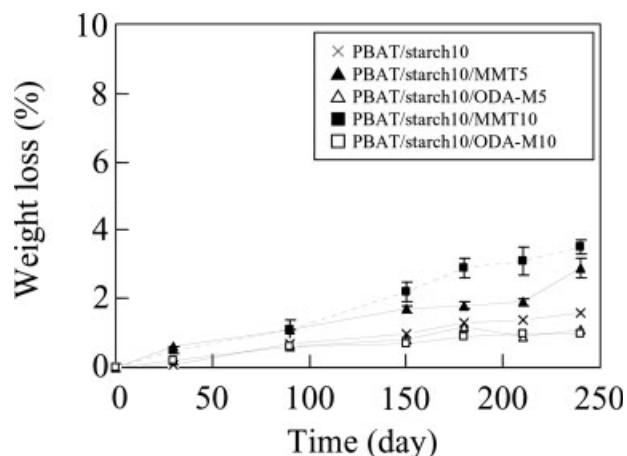


Figure 5 Weight loss of PBAT/starch10 and PBAT/starch10/clay after they were buried in soil.

and MMT. The composites with ODA-M had much less change than the composites with MMT.

Biodegradability of the PBAT composites in the aqueous medium containing activated sludge

Figure 8 shows the aerobic biodegradability determined by the measurement of BOD of thin-film samples composed of PBAT, starch, and clay in the aqueous medium containing activated sludge for 60 days. When the samples without starch are compared, the order of higher biodegradability is PBAT/MMT10 > PBAT \approx PBAT/ODA-M10, in agreement with the results from the burial in the soil. Regarding the samples containing 10 wt % starch, the order of higher biodegradability is PBAT/starch10/MMT10 \approx PBAT/starch10 > PBAT/starch10/ODA-M10. PBAT/starch20/MMT10 had the highest biodegradability of all the samples. The biodegradation of 54% for this composite after 60 days suggested that PBAT also biodegraded in addition to starch on the basis of the composition. In

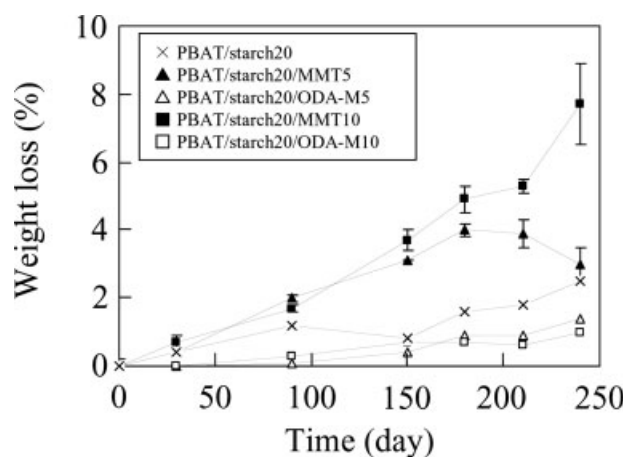


Figure 6 Weight loss of PBAT/starch20 and PBAT/starch20/clay after they were buried in soil.

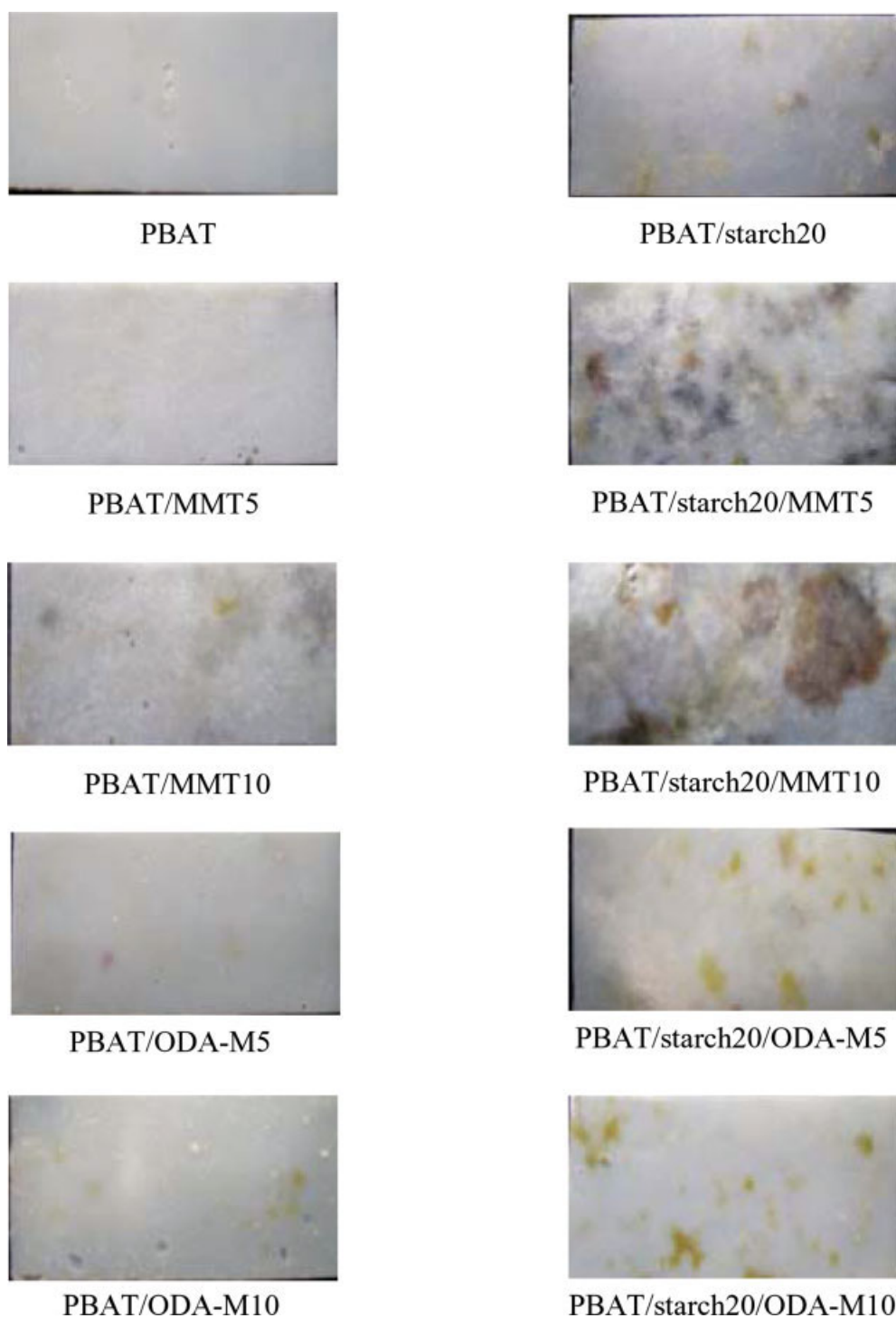


Figure 7 Optical photographs of PBAT, PBAT/starch, PBAT/clay, and PBAT/starch/clay samples after they were buried in soil for 240 days.

contrast to this result, the biodegradation of PBAT/starch20/ODA-M10 was about 22% at 40 days and very slowly increased afterward, suggesting a preferential decomposition of the starch component.

The promotion of the biodegradation due to the addition of MMT may be related to the highly hydrophilic character of MMT. On the other hand, the lower-

ing of the biodegradability for PBAT/ODA-M composites may have come from the finely dispersed silicate layers with large aspect ratios in the PBAT matrix, which forced enzyme or water diffusion in the bulk of the film through more tortuous paths. It is thought that the more hydrophobic character of ODA-M, in comparison with MMT, also contributed.

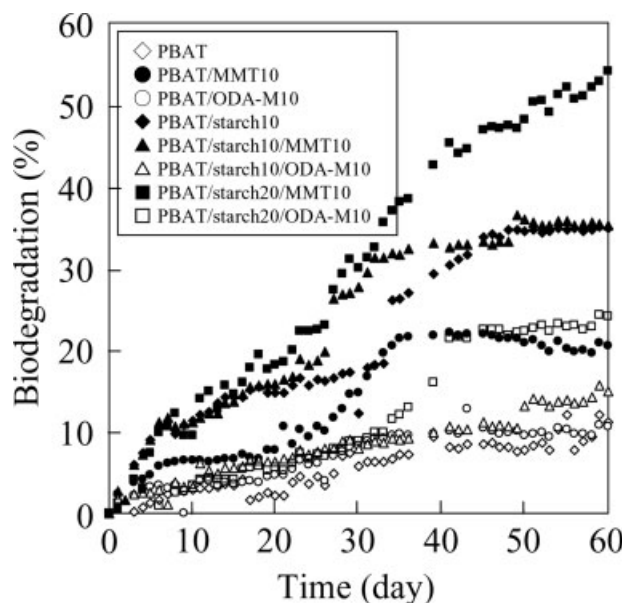


Figure 8 Biodegradability of PBAT, PBAT/clay, and PBAT/starch/clay determined by the measurement of BOD in an aqueous medium.

CONCLUSIONS

The biodegradability of PBAT and PBAT/starch composites with MMT and ODA-M prepared by melt intercalation was evaluated with aerobic biodegradability tests in soil and in an aqueous medium containing activated sludge. After they were buried in the soil for 8 months, the PBAT/MMT microcomposite exhibited a higher weight loss than the control PBAT, whereas the PBAT/ODA-M nanocomposites rather showed a lower weight loss. As for the effect of starch, the PBAT/starch20/MMT composites showed considerably higher weight loss than the corresponding PBAT/MMT composites. Also, the biodegradability test in the aqueous medium by the determination of BOD

showed that the addition of MMT and/or starch to PBAT promoted biodegradation, whereas the addition of ODA-M did not. It is thought that the hydrophilic character of MMT and starch promoted the biodegradation of PBAT, in addition to the biodegradation of starch itself, and that the formation of nanocomposites in the case of ODA-M depressed the diffusion of the substances that caused the biodegradation.

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