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Evaluation of biodegradation behavior of poly(butylene succinate-*co*-butylene adipate) with lowered crystallinity by thermally assisted hydrolysis and methylation-gas chromatography

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ABSTRACT

In our previous paper, thermally assisted hydrolysis and methylation-gas chromatography (THM-GC) measurements of poly(butylene succinate-*co*-butylene adipate) (PBSA) in the presence of tetramethylammonium hydroxide had revealed that the butylene adipate (BA) content in the PBSA films gradually decreased with soil burial degradation time. In order to clarify the cause of this change in copolymer composition, biodegradation behavior of PBSA with lowered crystallinity was evaluated by THM-GC. PBSA film samples with lower degree of crystallinity, prepared by heating and cooling quickly the original commercially available films, were subjected to a soil burial biodegradation test at 30 °C for up to 4 weeks. The copolymer compositions between BA and butylene succinate (BS) units in various stages of the degraded film samples were estimated on the basis of chromatograms obtained by THM-GC with less than 5% of the relative standard deviations. As a result, the change in copolymer composition for the heated PBSA films during soil burial was relatively small compared to the original films, suggesting that biodegradation for the heated films proceeded with the comparable rate for both BA and BS-rich moieties due to lowered crystallinity. Based on these results, the reason for the change in copolymer composition observed for the original PBSA films was clarified as follows: (1) the BA-rich moieties in the copolymer chains could show relatively lower crystallinity than the BS-rich moieties and (2) the BA-rich moieties were preferentially biodegraded during soil burial test, leading to the decrease in the BA content as the biodegradation proceeded.

1. Introduction

Poly(butylene succinate-*co*-butylene adipate) (PBSA), of which chemical structure is shown in Fig. 1, is one of the commercially available biodegradable aliphatic copolyesters [1,2]. PBSA has been widely used as packaging and container materials due to physical properties similar to those of commodity plastics such as polyethylene and polypropylene [3,4]. It is well known that various properties of PBSA, including biodegradability, are strongly affected by its copolymer composition. So far, various spectroscopic methods, such as NMR [5] and FT-IR [6], and conventional chromatographic techniques [7] have been utilized for compositional analyses of PBSA. However, these methods are not necessarily suited for routine analyses because of requirements of a relatively large sample size and cumbersome sample pretreatments.

On the other hand, it has been shown that thermally assisted hydrolysis and methylation-GC (THM-GC) in the presence of strong organic alkali such as a tetramethylammonium hydroxide (TMAH; $(CH_3)_4NOH$) is a rapid and precise technique for structural and compositional analyses of various condensation polymers [8–10]. This technique often provides extremely simplified and quantitative chromatograms mainly consisting of methyl derivatives of the constituent monomers in the polymer chains. Recently, the authors successfully applied the THM-GC to the compositional analysis of PBSA before and after the biodegradation only using trace amounts (ca. 20 μg) of the film samples [11]. The copolymer compositions of the PBSA samples were rapidly and precisely determined from the peak intensities of dimethyl succinate and dimethyl adipate derived from the butylene succinate (BS) and butylene adipate (BA) units, respectively, in the polymer chains through the THM reaction. Furthermore, it was revealed that the BA content in the film samples gradually decreased with soil burial degradation time, reflecting preferential biodegradation of the BA-rich moieties with the elapsed time of soil burial. Although the reason for this change

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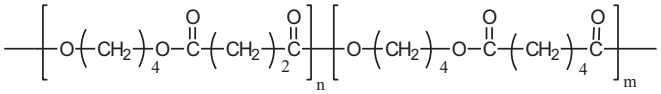

Fig. 1. Chemical structure of PBSA.

in copolymer composition during soil burial was not experimentally unraveled, local differences in biodegradability of a given PBSA film after soil burial were analyzed in detail based on the observed compositions [11].

Here, we presumed that the preferential degradation of the BA-rich moieties during soil burial might be explained by considering the effect of crystallinity of the PBSA sample on its biodegradation. So far, some researchers have attempted to evaluate the influence of crystallinity upon the biodegradation behavior of PBSA, focusing on the chemical structure and copolymer composition [5,12–15]. For example, Tserki et al. [14,15] reported that the degree of crystallinity was lowered by introducing BA units into a BS homopolymer, and became the lowest when the composition between the butylene succinate (BS) and the butylene adipate (BA) units was 40/60. Moreover, it was revealed that the highest enzymatic degradation rates was also observed at the copolymer composition of BS/BA = 40/60, reflecting the lowest degree of crystallinity. Ahn et al. examined the biodegradability for BS and BA homopolymers and a series of PBSAs with the BA content from 10 to 90% in the composting soils. As a result, biodegradability of the PBSA samples in the soils increased as the BA content in the copolymers increased from 10 to 60% due to the lowering of crystallinity [13].

These studies mentioned above suggest that the difference in crystallinity between the BS- and BA-rich moieties in the copolymer chains played an important role for the change in copolymer composition during biodegradation observed in our previous work [11]. The copolymer chains containing much amount of the BA units could show relatively lower crystallinity than the BS-rich chains. This feature in turn should lead to preferential biodegradation of the BA-rich moieties although the BS-rich chains must be hardly degraded due to their highly crystalline nature. One of the approaches to prove this assumption is to subject a PBSA film with lowered crystallinity even for the BS-rich moieties to the soil burial test, and trace the change in the copolymer composition during biodegradation. If the hypothesis is correct, the change in the copolymer composition is to be relatively small compared to the original PBSA film.

In this study, we tried to evaluate the biodegradation behavior of PBSA samples with lowered degree of crystallinity by means of THM-GC in order to clarify the reason for preferential degradation of the BA-rich moieties in original PBSA films during soil burial. Commercially available PBSA film samples and those with lower degree of crystallinity, prepared by heating and cooling quickly the original PBSA films, were subjected to a soil burial biodegradation test. Various stages of the degraded film samples were then analyzed by THM-GC in order to trace the change in the copolymer composition during the soil burial test. The observed difference in the change of the composition between the original and heated films was interpreted in terms of the biodegradation behavior of these PBSA films together with the observed weight loss during biodegradation.

2. Experimental

2.1. Materials

The film samples of commercially available PBSA (Bionolle 3001, Showa Denko Co. Ltd., Japan) were used in this work. It is known that a small amount (approximately 0.5%) of hexamethyl diisocynate units was introduced into the PBSA sample in order to elongate the polymer chains. The film samples with lower degree of crystallinity were prepared by heating the original ones at 80 °C for 20 min and subsequently cooling them quickly in iced water.

2.2. Soil burial biodegradation test

A soil burial degradation test of the original and heated PBSA films was carried out according to the procedure shown in our previous report [11]. Circle pieces (approximately 15 mg) of thin PBSA films (30 mm diameter, 35 μm thickness) were subjected to a soil burial biodegradation test for 1–4 weeks. The soil (pH 5.3) used in this study had been composted in the farm of Chubu University (Kasugai, Aichi Prefecture, Japan) and was contained in a small box in an incubator, in which the relative humidity was adjusted to approximately 90% and the temperature was kept constant at 30 °C. After designated periods, each degraded PBSA film was washed with water, dried, and weighed. The weight loss (weight %) of each degraded film was calculated from its dry weight normalized by that of the film sample before the burial test.

2.3. Differential scanning calorimetry (DSC) measurement

The DSC scans were recorded using a Bruker AXS DSC 3100 analyzer. About 10 mg of PBSA film samples was heated under a nitrogen flow of 20 ml/min. The temperature was programmed from 35 °C to 150 °C at a heating rate of 10 °C/min.

2.4. ^{1}H NMR measurement

^{1}H NMR spectra were obtained on a JEOL AL400 (400 MHz) spectrometer under the following conditions; spectral width of 8000 Hz, acquisition time of 4 s, relaxation time of 3 s and pulse width of 8.5 μs. About 5 mg of a sample dissolved in $CDCl_3$ (0.7 ml) was measured at room temperature. Chemical shifts were recorded in parts per million relative to the standard tetramethylsilane. The accumulation of 32 scans was used to obtain ^{1}H NMR spectra having sufficient S/N values for the sample.

2.5. THM-GC measurement

The THM-GC system used in this study was basically the same as that described in our previous paper [11]. A microfurnace pyrolyzer (Frontier laboratories, PY-2010D) was attached to a GC (Agilent, HP 4890) equipped with a flame ionization detector (FID). The small platinum cup (2 mm i.d. × 4 mm height) containing 2 μl of the chloroform solution (10 mg/ml) of each film sample together with 2 μl TMAH solution (2.2 M in methanol, Aldrich) was dropped in the center of a pyrolyzer heated at 350 °C under a helium carrier gas flow (50 ml/min). A part of the flow (1 ml/min) reduced by a splitter was introduced into a metal capillary separation column (Frontier Laboratories, Ultra ALLOY-5 (MS/HT); 30 m long × 0.25 mm i.d.) coated with immobilized 5% diphenyl-95% dimethylpolysiloxane (1.0 μm film thickness). The column temperature was programmed from 50 °C to 300 °C at a rate of 5 °C/min. Identification of the peaks on the chromatograms was carried out by using a THM-GC-mass spectrometry (MS) system (Shimadzu, QP-5050 with an electron ionization (EI) sources).

3. Results and discussion

Fig. 2 shows the DSC thermograms of (a) the original and (b) heated PBSA film samples before biodegradation test. From the areas of melting endothermic peaks observed in these thermograms, the measured values of the heat of fusion were estimated to