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A novel evaluation method for biodegradability of poly(butylene succinate-*co*-butylene adipate) by pyrolysis-gas chromatography

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Abstract

Biodegradation behavior of poly(butylene succinate-*co*-butylene adipate) (PBSA) film samples during the soil burial degradation test was studied by pyrolysis-gas chromatography (Py-GC). In the pyrograms of the PBSA film sample residues, various ester compounds containing succinate and/or adipate units were observed as the main pyrolysis products along with some minor pyrolyzates such as fatty-acid esters comprising propionates and valerates which might be formed mostly from carboxyl end-groups existing in PBSA molecules. Although the relative yields of the major pyrolyzates were almost unchanged before and after the soil burial test, those of the fatty-acid esters decreased with the soil burial time almost correlating with the decrease in recovery as residue. Thus, the variation of the relative yields of the fatty-acid esters proved to be a good measure to evaluate the degree of PBSA biodegradation. Furthermore, the local structural changes for the biodegraded PBSA film samples were also evaluated from the relative yields of these specific esters observed on the pyrograms for tiny pieces of analyte (ca. 0.1 mg) sampled from local points.

Keywords: Poly(butylene succinate-*co*-butylene adipate); Pyrolysis-gas chromatography; Biodegradation; Evaluation method

1. Introduction

With the recent raise of the consciousness to waste management and global environmental preservation, it has been recognized that biodegradability is one of the important functions for polymeric materials in practical use. Therefore, much interest has been paid for synthesis and/or modification of biodegradable polymers such as poly(3-hydroxyalkanoate)s, poly(lactic acid), poly(butylene succinate), and so on [1–7].

Biodegradabilities of these polymeric materials have been examined by various approaches involving enzymatic degradation in vitro, microbial degradation with cultured microorganisms, and environmental degradation by exposing them to realistic environment, e.g. burial in soil or immersion in natural water [1–8]. Among these, a soil burial degradation test has been used as a traditional method because of its similarity to actual conditions of waste disposal. After the soil burial degradation test, the biodegradation of the polymeric materials is usually evaluated by various ways including determination of weight loss (or recovery), measurement of changes in polymer properties such as tensile strength, microscopic and/or visual inspection of the growth of microorganisms on the polymer surface, and measurement of changes in average molecular weight and molecular weight distribution [1,2,4]. However, these methods give little information about the changes in chemical structures of the starting materials during biodegradation which might provide good clue to design new excellent biodegradable materials.

In general, the chemical structures of polymeric films are routinely characterized by spectroscopic methods

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such as Fourier transform infra-red absorption spectroscopy (FT-IR). However, biodegraded polymer films recovered after the soil burial degradation test are often difficult to be characterized in detail by FT-IR because infrared ray might scatter on the film surface roughly eroded by microorganisms to cause poor sensitivity and resolution. On the other hand, pyrolysis-gas chromatography (Py-GC) has been utilized as a highly sensitive, rapid and convenient technique to elucidate microstructures of various polymeric materials using only trace amounts (ca. 0.1 mg or less) of polymer samples in any form [9]. So far the thermal degradation mechanisms of some biodegradable polyesters such as poly(3-hydroxybutyrate) (PHB) [10] and poly(lactic acid) (PLA) [11] have been investigated by Py-GC. In these reports, it was demonstrated that PHB decomposed predominantly according to *cis*-elimination mechanism to form 2-butenoic acid along with some oligomeric products, whereas PLA decomposed mainly through intramolecular transesterification to form cyclic oligomers. These Py-GC studies, however, have not been concerned with the structural characterization of the biodegradable polyesters.

In this study, changes in the chemical structures of a biodegradable aliphatic copolyester, poly(butylene succinate-*co*-butylene adipate) (PBSA), during the soil burial degradation test were investigated by Py-GC. Variations in the yields of characteristic pyrolysis products were correlated with the degree of biodegradation of PBSA. Furthermore, this technique was applied to elucidate the local variation of biodegradation in a PBSA film after soil burial.

2. Experimental

2.1. Materials

Industrially available biodegradable copolyester, poly(butylene succinate-*co*-butylene adipate) (PBSA) with the trade name Bionolle 3001 (Showa Highpolymer Co. Ltd., Japan), was subjected to the soil burial biodegradation test. Fig. 1 shows the possible chemical structure of the PBSA sample. The PBSA main chains are composed of butylene succinate and butylene adipate units which are randomly linked each other, and both ends of the polymer chain are to be mainly terminated by hydroxyl groups [12–14]. In addition, in order to elongate the PBSA chains, the hydroxyl end groups of lower molecular weight prepolymers were coupled through a small amount of hexamethylene diisocyanate [12,13]. Furthermore, the presence of oligomers with alcohol and carboxyl as end-groups was also verified to some extent by Carroccio et al. using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [15].

The composition of the original PBSA before the soil burial degradation test was estimated by ^{1}H NMR: the molar ratio of the succinate unit to the adipate unit was ca. 4:1, and the content of the coupling agent (hexamethylene diisocyanate) unit was ca. 0.5 mol%. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the original PBSA estimated by size exclusion chromatography (SEC) were 4.6×10^4 and 1.97, respectively.

2.2. Soil burial degradation test

The soil burial degradation test of PBSA films was carried out as described in the previous papers [16–18]. In order to correlate the yields of pyrolysis products from PBSA films with the period of the soil burial degradation test, four pieces of the thin PBSA films (20×10 mm, 35 μm thickness, weighing ca. 7.5 mg) were buried in soil for 10, 20, 30, and 60 days, respectively. The soil (pH 6.8, water content ca. 25%) used in this study had been composted for more than 10 years in the farm of Nagoya University (Nagakute, Aichi, Japan), and was contained in a dark box placed in a desiccator, in which the relative humidity was adjusted to 60–70% and temperature was thermostated at 27°C. After designated periods, each recovered film was washed with water, dried in vacuo, and weighed. Each film sample (recovery 55–96 wt.%) was then divided into two pieces: one was used for Py-GC measurements, while the other was dissolved in chloroform for SEC measurements.

Furthermore, in order to evaluate the local variation of biodegradation in a degraded PBSA film, a larger size of PBSA film (30×30 mm, 35 μm thickness, ca. 40 mg) was buried in the soil for 10 days according to the basically the same procedure mentioned above (recovery 61 wt.%).

2.3. Size exclusion chromatography (SEC) measurement

SEC measurements were carried out with a Tosoh HLC8020 liquid chromatograph equipped with a refractive index detector which was operated with Tosoh G-5000H_{XL}, G-3000H_{XL}, and G-2000H_{XL} columns

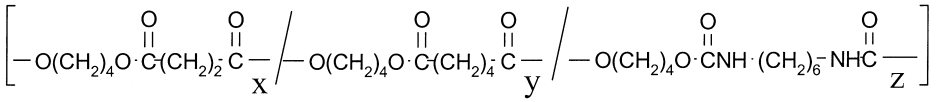


Fig. 1. Possible chemical structure of PBSA. ($x/y/z = 79.7/19.8/0.5$ determined by ^{1}H NMR).

connected in series. All SEC experiments were performed at 38°C using chloroform as the mobile phase (1 ml/min). Injection volume of the sample solution with the polymer concentration of ca. 5 mg/ml was 100 μl. The values of M_n and M_w/M_n were calculated with the calibration curve generated using polystyrene standards.

2.4. Pyrolysis-gas chromatography (Py-GC) measurement

The Py-GC system used in this study was basically the same as described in our previous paper [19]. A microfurnace pyrolyzer (Frontier Lab, PY-2010D) was attached to a GC (Hewlett Packard, HP-6890) equipped with a flame ionization detector (FID). The platinum sample cup containing about 0.1 mg of a given sample was dropped into the center of the pyrolyzer heated at 500°C under helium carrier gas (50 ml/min). A part of the flow (1 ml/min) reduced by a splitter was introduced into a fused silica capillary separation column (Hewlett Packard, PONA; 50 m long×0.20 mm i.d.) coated with immobilized polydimethylsiloxane (0.5 μm film thickness). The column temperature was set at 50°C for 5 min, then programmed up to 300°C at a rate of 5°C/min, and held at 300°C for 15 min. Identification of the peaks on the pyrograms was carried out mainly using a gas chromatography–mass spectrometry (GC–MS) system (Jeol, AM-II 150) with an electron impact ionization (EI) at 70 eV or a chemical ionization (CI) using 2-methylpropane as a reagent gas, to which the pyrolyzer was also attached.

3. Results and discussion

3.1. Recovery and molecular weight change of PBSA samples after the soil burial degradation test

Table 1 summarizes recovery (wt.%), and M_n and polydispersity index (M_w/M_n) determined by SEC of the PBSA film samples before and after the soil burial degradation test. With the elapse of the burial time, the film samples gradually degraded, and the recovery of the film fell to 55% after the soil burial for 60 days. Here, it should be noted that the M_n values of the residual samples slightly increased after the soil burial test up to 20 days, while the polydispersity indices monotonously decreased. These facts suggest that smaller molecules in the film sample might degrade preferentially in the earlier stage mainly through exo-type biodegradation in which polymer chains are almost completely degraded from the chain ends.

Table 1
Recovery (wt.%) and molecular weight variation of the biodegradable polyester sample before and after the soil burial degradation test

Time (days)	Recovery (wt.%)	Molecular weight[a]	
		M_n ($\times 10^{-4}$)	M_w/M_n
0	100	4.6	1.9_7
10	96	5.8	1.8_1
20	80	7.1	1.6_7
30	73	6.3	1.4_7
60	55	6.5	1.3_9

[a] Determined by SEC.

3.2. Pyrolysis of the control PBSA sample

Fig. 2 shows a typical pyrogram of the control PBSA film sample observed by Py-GC at 500°C. The assigned peaks in the pyrogram are listed in Table 2 together with their origins and effective carbon numbers (ECN) corresponding to the relative molar sensitivities for the FID [20]. The major products observed on the pyrogram are various ester compounds containing a succinate unit ($\mathbf{S}_x$) and an adipate unit ($\mathbf{A}_x$), and succinate dimers ($\mathbf{SS}_x$) and hybrid dimers ($\mathbf{SA}_x$). In addition, various low-molecular weight products such as butene (**B**), tetrahydrofuran ($\mathbf{T}_{HF}$), and butadiene ($\mathbf{B}_D$) originating from 1,4-butandiol unit, and cyclopentanone ($\mathbf{C}_P$) from the adipate unit are also detected. Although most of the ester compounds have hydroxyl and/or vinyl end groups, the mono-carboxylic acid esters having an alkyl end group (i.e. fatty-acid esters) such as propionates ($\mathbf{P}_x$) and valerates ($\mathbf{V}_x$), which might be derived from the succinate and adipate units, respectively, are also observed as minor products. In addition, a small amount of hexamethylene diisocyanate (**H**) is clearly detected, which may be derived from the isocyanate unit corresponding to the coupling agent. These pyrolysis products, except those relating to succinate unit, have already been reported in the previous Py-GC work [21] on the polyurethane sample composed of poly(butylene adipate) (PBA) type polyol and hexamethylene diisocyanate, which are reported to degrade primarily through a six-membered transition state around ester

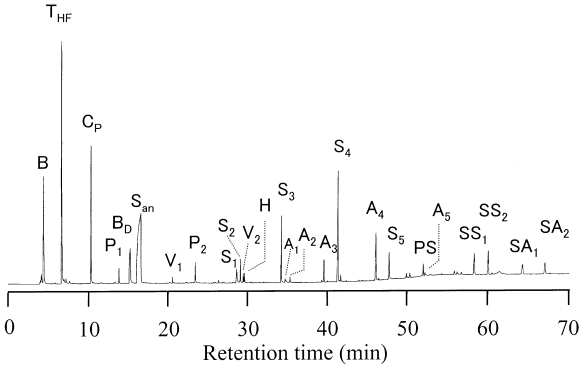
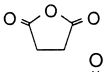


Fig. 2. Typical pyrogram of PBSA at 400°C. Peak assignments are listed in Table 2.

Table 2
Identification of the characteristic peaks on the pyrograms shown in Figs. 2 and 3

Peak	Structure	MW	Origin[a]	ECN[b]
B	$CH_2=CHCH=CH_2$	54	B	3.80
T_{HF}		72	B	3.20
C_P		84	A	4.20
P_1	$CH_3CH_2CO(CH_2)_2CH=CH_2$	128	B+S	5.65
B_D	$HO(CH_2)_4OH$	90	B	2.80
S_{an}		100	S	1.95
V_1	$CH_3(CH_2)_3CO(CH_2)_2CH=CH_2$	156	B+A	7.65
P_2	$CH_3CH_2CO(CH_2)_4OH$	146	B+S	5.15
S_1	$HOC(CH_2)_2CO(CH_2)_2CH=CH_2$	172	B+S	5.25
S_2	$-OC(CH_2)_2CO(CH_2)_4-$	172	B+S	5.50
V_2	$CH_3(CH_2)_3CO(CH_2)_4OH$	174	B+A	7.15
H	$OCN(CH_2)_6NCO$	168	H	6.00[c]
S_3	$CH_2=CH(CH_2)_2OC(CH_2)_2CO(CH_2)_2CH=CH_2$	226	B×2+S	9.30
A_1	$HOC(CH_2)_4CO(CH_2)_2CH=CH_2$	200	B+A	7.25
A_2	$-OC(CH_2)_4CO(CH_2)_4-$	200	B+A	7.50
A_3	$CH_2=CH(CH_2)_2OC(CH_2)_4CO(CH_2)_2CH=CH_2$	254	B×2+A	11.30
S_4	$CH_2=CH(CH_2)_2OC(CH_2)_2CO(CH_2)_4OH$	244	B×2+S	8.80
A_4	$CH_2=CH(CH_2)_2OC(CH_2)_4CO(CH_2)_4OH$	272	B×2+A	10.80
S_5	$HO(CH_2)_4OC(CH_2)_2CO(CH_2)_4OH$	262	B×2+S	8.30
PS	$CH_3CH_2CO(CH_2)_4OC(CH_2)_2CO(CH_2)_4OH$	318	B×2+S+A	12.65
A_5	$HO(CH_2)_4OC(CH_2)_4CO(CH_2)_4OH$	290	B×2+A	10.30
SS_1	$-OC(CH_2)_2CO(CH_2)_4OC\cdot(CH_2)_2CO(CH_2)_4-$	344	B×2+S×2	11.00
SS_2	$CH_2=CH(CH_2)_2OC(CH_2)_2CO(CH_2)_4OC\cdot(CH_2)_2CO(CH_2)_2CH=CH_2$	398	B×3+S×2	14.80
SA_1	$-OC(CH_2)_2CO(CH_2)_4OC\cdot(CH_2)_4CO(CH_2)_4-$	372	B×2+S+A	13.00
SA_2	$CH_2=CH(CH_2)_2OC(CH_2)_2CO(CH_2)_4OC\cdot(CH_2)_4CO(CH_2)_2CH=CH_2$	426	B×3+S+A	16.80

[a] B, 1,4-butanediol moiety; A, adipic acid moiety; S, succinic acid moiety; H; hexamethylene diisocyanate moiety.
[b] The effective carbon number; molar correction factor for FID.
[c] Determined experimentally.

linkages to give a pair of a carboxylic acid and an olefinic fragment as shown in Scheme 1.

The formation of acidic and/or olefinic end groups such as **B** and $\mathbf{A}_x$ (except for $\mathbf{A}_2$) can be explained through this mechanism. Because basically the same type of the thermal cleavage might occur to some extent during the melt polycondensation reaction to form PBSA, a certain amount of acidic and/or olefinic end groups would exist in the original PBSA even before biodegradation [15]. Furthermore, valerates ($\mathbf{V}_x$) are to be produced during the pyrolysis of PBSA through decarboxylation at the acidic end of the larger fragments as shown in Scheme 2 [21].

On the other hand, cyclic compounds such as A_2 should be formed through intramolecular transesterification, as shown in Scheme 3 [10,11].

As for the succinate units in the PBSA chain, similar degradation reactions mentioned above (Schemes 1–3) should also occur to form the corresponding products such as $\mathbf{S}_x$, $\mathbf{P}_x$, and $\mathbf{SS}_x$ as well as hybrid dimers such as **PS** and $\mathbf{SA}_x$ comprising both succinate and adipate units.

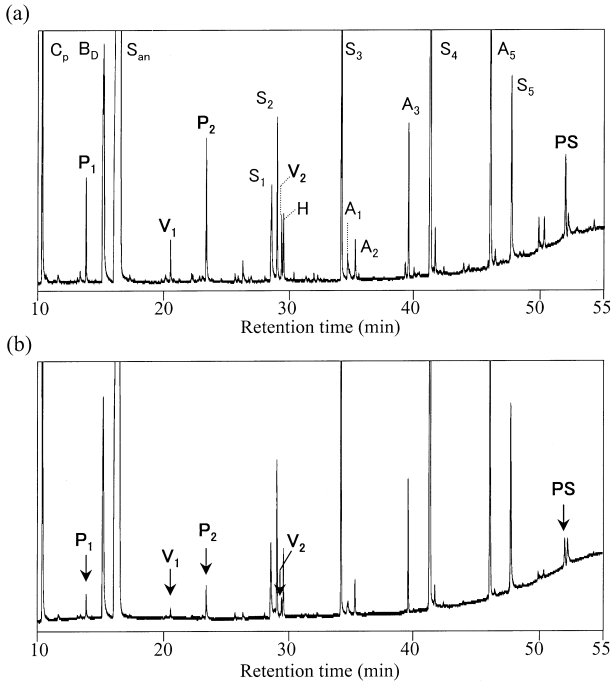
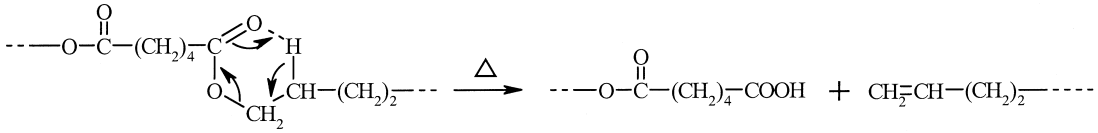


Fig. 3. Expanded pyrograms of PBSA at 400°C; (a) the control polymer sample and (b) the sample recovered after soil burial for 60 days. Peak assignments are listed in Table 2.

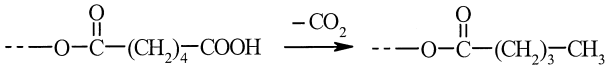
3.3. Pyrolysis of the PBSA samples after the soil burial degradation test

Fig. 3 shows the expanded pyrograms of (a) the control PBSA film sample and (b) the film recovered after the soil burial for 60 days. In spite of much similarity between the pyrograms of the PBSA samples before and after the soil burial, it is interesting to note that the relative peak intensities of the fatty-acid esters such as propionates ($\mathbf{P}_x$) and valerates ($\mathbf{V}_x$) are considerably decreased after the soil burial as denoted by arrows in the bottom pyrogram. This observation suggests that the chemical structure of the PBSA chains would slightly change with the progress of biodegradation. Here, changes in the yield of these characteristic products with the elapsed time of the soil burial test were examined in detail in order to investigate the structural changes of PBSA during biodegradation.

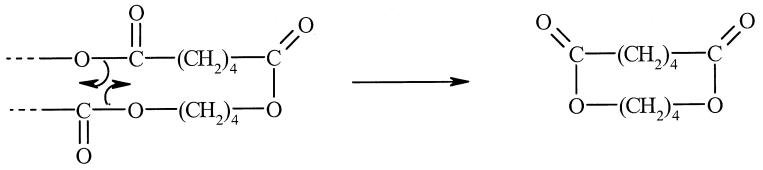
The observed intensity of peak x (I_x) was firstly converted into the corrected peak intensity (C_x) corresponding to the relative molar amount of each compound by making molar sensitivity corrections for FID using the ECN values shown in Table 2:



Scheme 1.



Scheme 2.



Scheme 3.

$$C_x = I_x/ECN_x \quad (1)$$

Therefore, the total molar yields Y_S, Y_A, and Y_H for the succinate, adipate and hexamethylene diisocyanate units, respectively, in the observed pyrolysis products, are expressed as follows:

$$Y_S = \sum_i \left[C_{S_i} + C_{S_{an}} + C_{P_i} + 2C_{SS_i} + 2C_{PS} + C_{SA_i}\right] \quad (2)$$

$$Y_A = \sum_i \left[C_{A_i} + C_{V_i} + C_{SA_i} + C_{C_p}\right] \quad (3)$$

$$Y_H = C_H \quad (4)$$

Accordingly, the relative molar composition for each unit is defined as follows:

$$S(\text{mol\%}) = [Y_S/(Y_S + Y_A + Y_H)] \times 100 \quad (5)$$

$$A(\text{mol\%}) = [Y_A/(Y_S + Y_A + Y_H)] \times 100 \quad (6)$$

$$H(\text{mol\%}) = [Y_H/(Y_S + Y_A + Y_H)] \times 100 \quad (7)$$

Firstly, the changes in the relative yields of succinate and adipate units (S mol% and A mol%) in the copolymer type PBSA with the elapsed time of the soil burial test were examined based on the data calculated by Eqs. (5) and (6). In a previous paper as for the corresponding homopolymers, poly(butylene adipate) (PBA) and poly(-butylene succinate) (PBS), it was reported that the degradation rate of PBA was faster than that of PBS [22]. For the copolymer type PBSA used in this study, however, both the relative yields of the products from succinate and adipate units proved to be almost constant (ca. 13% and ca. 85%, respectively) for the residue throughout the soil burial test. This fact suggests that both succinate and adipate units have almost comparable biodegradability.

The biodegradability of urethane linkages was then examined using the data calculated by Eq. (7). Fig. 4 shows the change in the relative yields of hexamethylene diisocyanate (H mol%) with the soil burial time. The observed values of the yields slightly increased up to 20 days caused by the soil burial degradation, and thereafter remain almost constant. This fact partly supports sluggish biodegradation at urethane linkages as was previously reported [23,24].

On the other hand, as was mentioned previously, relative yields of the fatty-acid esters such as propionates ($\mathbf{P}_x$) and valerates ($\mathbf{V}_x$) apparently decreased in the pyrograms after the soil burial test as shown in Fig. 3. Here, the molar yields for the fatty-acid esters (Y_{FAE}) are expressed as follows:

$$Y_{FAE} = \sum_i \left[C_{P_i} + C_{V_i} + C_{PS}\right] \quad (8)$$

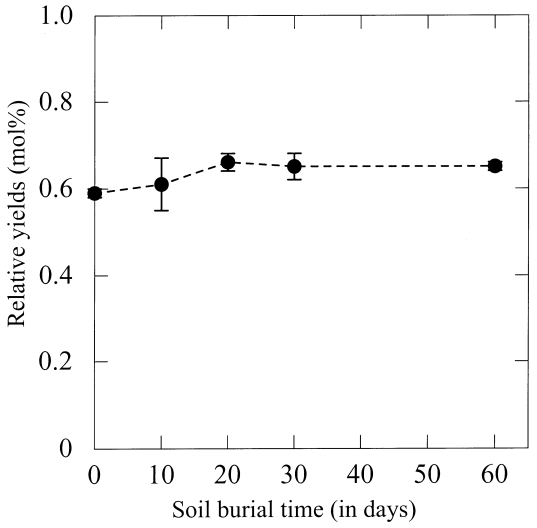


Fig. 4. Change in the relative yields of the products from hexamethylene diisocyanate (HMDI) originating from the diisocyanate unit.

Thus, the relative yields of the fatty-acid esters are defined as follows:

$$FAE(\text{mol\%}) = [Y_{FAE}/(Y_S + Y_A + Y_H)] \times 100 \quad (9)$$

Fig. 5 shows the observed FAE (mol%) of the film samples as a function of the soil burial time together with the residue recovery in wt.%. The relative yields of the fatty-acid esters gradually decrease with the soil burial time almost correlating with the decrease in recovery. This phenomenon demonstrates that the variation of the relative yields of the fatty-acid esters can be a good measure to evaluate the degree of biodegradation of PBSA. The decrease in the relative yields of the fatty-acid esters might be correlated with the preferential biodegradation at carboxyl end-groups in the

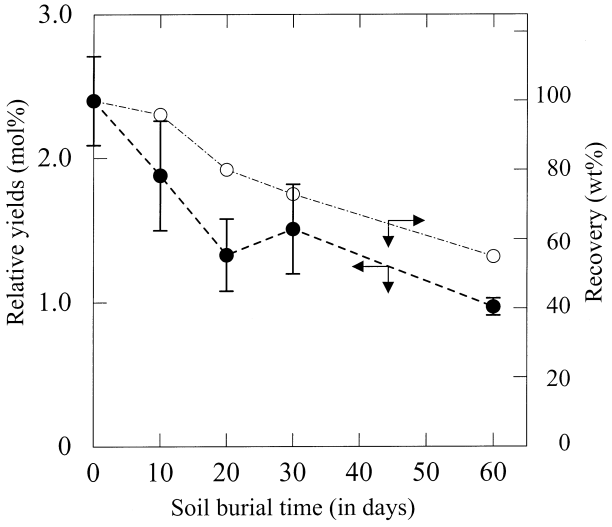


Fig. 5. Changes in the relative yields of the fatty-acid ester products during soil burial (●) together with recovery of the film samples (○).

PBSA chains. These end-groups would exist at much higher concentration in the lower molecular weight portions of the PBSA sample and might decompose into propionates or valerates through decarboxylation. However, detailed interpretation for the formation mechanisms of the fatty-acid esters is still under investigation.

3.4. Evaluation of local biodegradation for a given degraded film sample

Since Py-GC can generally be performed using only trace amounts (ca. 0.1 mg or less) of sample, it was applied to study local biodegradation on a degraded PBSA film sample. In this case, the degree of biode-

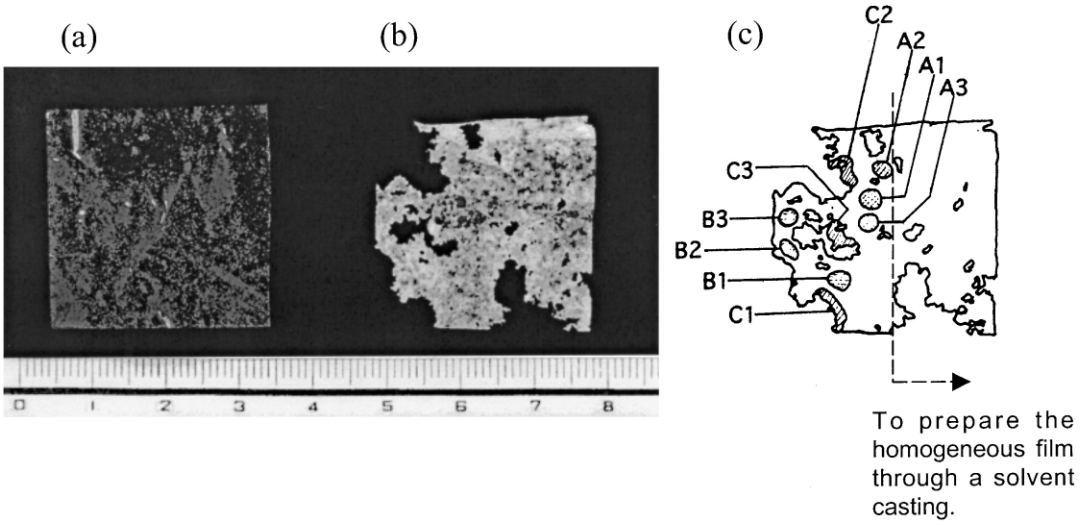


Fig. 6. Photographs of the PBSA film samples; (a) the original polymer sample and (b) the sample recovered after the soil burial for 10 days, together with (c) the illustration of the sampling points corresponding to the photograph (b) for the Py-GC measurements.

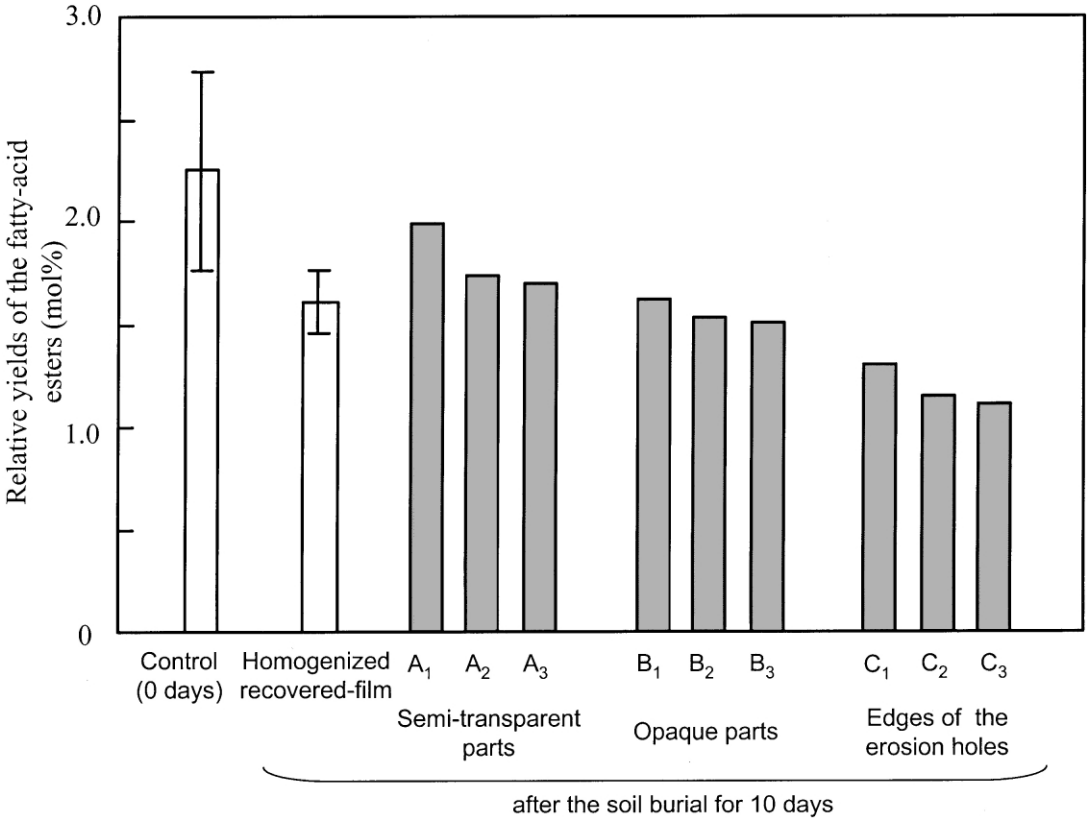


Fig. 7. Evaluation of the local biodegradation using relative yields of the fatty-acid esters for the biodegraded sample recovered after the soil burial for 10 days. The sampling points are shown in Fig. 6.

gradation at a local point in a given film sample was evaluated based on the relative yield of the fatty-acid esters in the observed pyrogram as was described in the previous section. Here, to clarify the heterogeneity in biodegradation, a relatively larger PBSA film (30×30 mm) subjected to the soil burial degradation test for 10 days was used. Fig. 6 shows photographs of (a) the control PBSA film before the soil burial, and (b) the film recovered after the soil burial for 10 days, together with (c) an illustration of the sampling points on the recovered film for the Py-GC measurement. The degraded film mostly became opaque with forming many holes caused through erosion by microorganisms, although semi-transparent parts can be still observed partially around the center of the film. In order to elucidate the local variation of biodegradation on the unevenly degraded film by Py-GC, tiny pieces (ca. 0.1 mg) were sampled from the semi-transparent parts ($\mathbf{A_1}$–$\mathbf{A_3}$), the opaque parts ($\mathbf{B_1}$–$\mathbf{B_3}$), and the edges of the eroded holes ($\mathbf{C_1}$–$\mathbf{C_3}$) as shown in Fig. 6c. Additionally, a homogenized recovered film sample was prepared through solvent cast using the right half of the originally recovered film shown in Fig. 6c to estimate the average degree of biodegradation by Py-GC.

Fig. 7 shows the relative yields of the fatty-acid esters observed in the pyrograms of the degraded film sampled at various sampling points together with those for the homogenized recovered-film and for the undegraded control film. As was expected from the appearances, the yields of the fatty-acid esters are significantly lower for the homogenized film sample than that for the control one, and the value for every point also decreases with the order the semi-transparent parts ($\mathbf{A_1}$–$\mathbf{A_3}$) > the opaque parts ($\mathbf{B_1}$–$\mathbf{B_3}$) > the edges of the eroded holes ($\mathbf{C_1}$–$\mathbf{C_3}$). This result demonstrates that Py-GC can be applied to elucidate the local variation of biodegradation in a given biodegraded film sample.

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