

# Biodegradation of Low-Density Polyethylene, Polystyrene, Polyvinyl Chloride, and Urea Formaldehyde Resin Buried Under Soil for Over 32 Years

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## SYNOPSIS

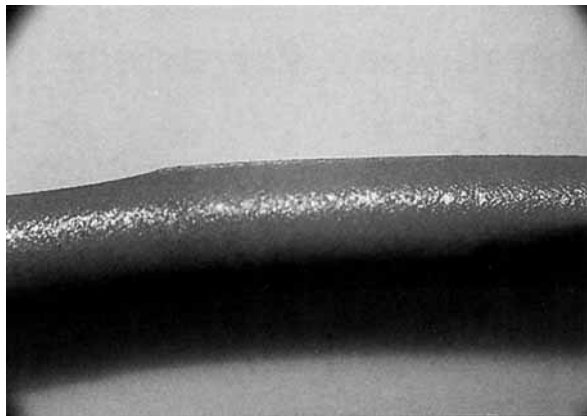
The biodegradation of several polymers that had been buried under soil for over 32 years was examined. No evidence of biodegradation was found for polystyrene, polyvinylchloride, and urea formaldehyde resin. A remarkable degradation was indicated for low density polyethylene thin films which were directly in contact with soil. Severely degraded parts of the film is characterized by whitening. Many small holes were recognized on the surface of the whitened part. The whitened part is specific for the growth of hyphae. FT-IR spectra of the whitened part showed a characteristic band in the vicinity of  $1640\text{ cm}^{-1}$  which was assigned to the stretching vibration of C=C bond. Although the part which was not in contact with soil was clear, it also showed evidence of degradation from the presence of carbonyl band in FT-IR. It was suggested that the degradation of the clear part is due to the usual thermo-oxidative process, while the degradation of the whitened part is due to the biotic process. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Generally, synthetic polymers such as polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), and urea formaldehyde resin (UF) are classified as nonbiodegradable plastics. Several investigators have attempted to degrade these polymers under bioactive conditions. For instance, the biodegradability of PS was examined in soil or in activated sludge, but no evidence of degradation was observed even after long time treatment.<sup>1,2</sup> As for PVC, the added plasticizer was recognized to degrade, but no change was observed for PVC polymer itself.<sup>3</sup> Although oligomeric PE with molecular weight around 1000 was reported to undergo microbial degradation,<sup>4</sup> it is generally accepted that high-molecular-weight PE is not biodegradable.<sup>5</sup> These plastics have been used as inexpensive packaging materials since

the early 1950s. Accordingly, the maximum period that these plastics have undergone oxidative degradation under bioactive soil is at most 30–40 years. Thus, it is inevitable that no systematic investigation has been carried out to investigate the long-term biodegradability of these plastics. As far as we know, the longest test period for the investigation of the biodegradation of synthetic polymers may be about 10 years carried out for low-density PE (LDPE) by Albertsson and Karlsson.<sup>6</sup> They used LDPE films labeled with  $^{14}\text{C}$ , cut them into small pieces, and buried them under soil, which was kept in controlled conditions. The degree of biodegradation was estimated by the yield of  $^{14}\text{CO}_2$ , which is the possible final product of the metabolic cycle of the degradation of the LDPE. Although their investigation was epoch-making, because they showed clear evidence for the biodegradation of high-molecular-weight LDPE, their test period was too short to estimate the practical degradation life of LDPE and the degree of degradation was too small to detect

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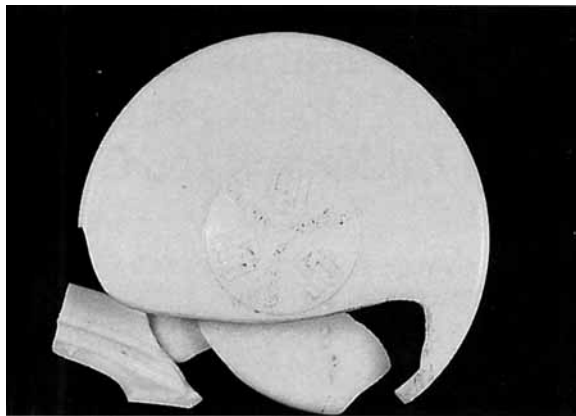


**Figure 1** Electric cable: PVC.

the change in the material properties of LDPE due to degradation.

In order to estimate the material life of polymers which undergo oxidative degradation, we often use an accelerated test. This test is based on the assumption that the oxidative degradation is an activated process. In general, it requires long extrapolation from high-temperature data to obtain the room temperature life of oxidation. As for the biodegradation, however, the oxidation proceeds via an enzymatic process with very low activation energy which is only possible for mild conditions around room temperature. Thus it is practically impossible to apply the accelerated test to biodegradation, and it is necessary to carry out long-term degradation tests under model conditions which are similar to that of a practical system. As it was not practical for us to carry out the long-term field test, we tried to find plastic materials which had been buried under soil for very many years.

We have fortunately found LDPE, PS, PVC, and UF which were buried under bioactive soil. More-



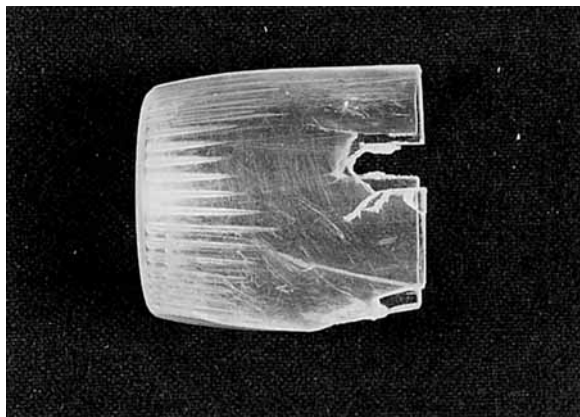
**Figure 3** Cup of makeup jar: UF.

over, we can estimate that the period that these plastics were buried under soil is 32–37 years, because we were able to specify by chance the time when these plastics were discarded under soil. As far as we know, this is the longest test period for the biodegradation of plastic materials. Here, we show the careful analysis of these samples as well as the analysis of the soil. The results are focused on LDPE, which seems to be most susceptible to biodegradation among these plastic materials.

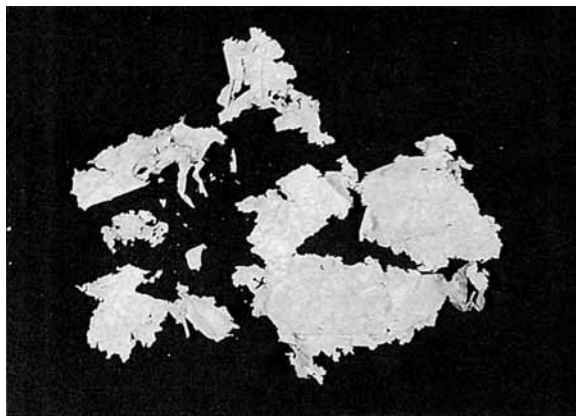
## EXPERIMENTAL

### Sampling Site

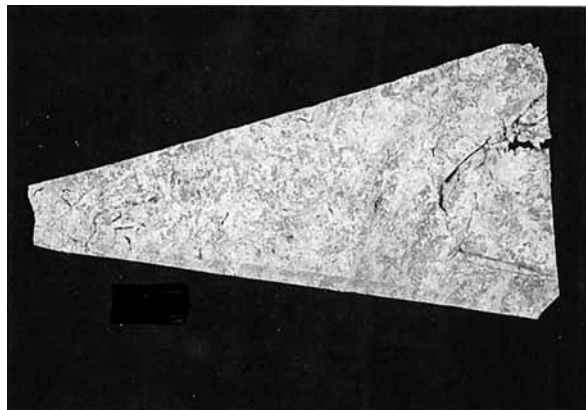
Sampling was carried out under garden soil located in Ibaraki Prefecture, Japan. The samples were collected under about 10 and 50 cm depth from the surface, respectively. The appearances of the samples are shown in Figures 1–6. Figure 1 shows part of a PVC electric wire with 45 cm of total length



**Figure 2** Premium cup for whiskey bottle: PS.



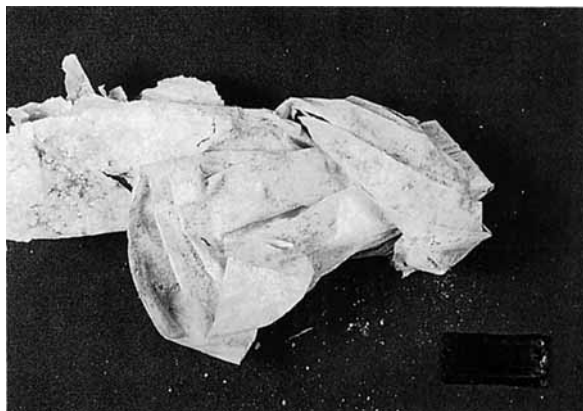
**Figure 4** LDPE fragments (sample 1).



**Figure 5** Triangular film bag for juice (sample 2).

and 3 mm diameter. About 4 mg of thin sections were cut both from the surface and from about 1 mm depth from the surface. Figure 2 shows a PS small cup of about 3.5 cm height and 2.5 cm diameter. The cup was transparent and its total weight was 5.0 g. Figure 3 shows a UF makeup jar of about 3 cm diameter. The total weight of this jar was about 12 g. Thin sections were also cut both from the surface and from about 1 mm depth from the surface. Figure 4 shows small LDPE fragments with average thickness of about 60  $\mu\text{m}$ . Figure 5 shows a LDPE triangular juice bag. The three sides of the triangle were about 12, 12, and 9 cm, respectively, and total weight was about 2 g. Figure 6 shows a LDPE tied film with a size of about 25  $\times$  28 cm when it was opened (See Fig. 7). The total weight of the film was about 4 g and the thickness was about 60  $\mu\text{m}$ .

The characterization of these samples was carried out by infrared spectroscopy, pyrolysis gas chromatography, and differential scanning calorimetry. The analysis of LDPE samples was carried out with a virgin LDPE film (F31N, from Nippon Petro-



**Figure 6** Tied film (sample 3).



**Figure 7** Opened film of sample 3.

chemicals Co. Ltd.) as a control sample. The standard sample for PS was TPX resin (Mitsui Petrochemicals Co. Ltd.). Since the PVC electric wire and the UF jar seem to contain many additives, we could not use any standard polymer samples to estimate the degree of degradation. Therefore, we only compared the analytical results of thin sections cut from the extreme surface and from 1 mm depth.

The period of burial was determined to be 32–37 years for the following reasons. It became apparent that the disposal of waste plastics in this site was continued from 1955 to 1960. In addition, we found, for the LDPE film bags, the manufacturer and the date of manufacture.

#### Identification of Bacteria and Chemical Analysis of Soil

In order to clarify the kind and the number of bacteria associated with biodegradation, they were extracted by phosphate buffer from the garden soil and incubated for 48 h at 35°C on standard broth agar. Endospore sulfite reducing anaerobes were incubated under the same conditions on clostridium agar, while eumycetes were incubated for 7 days at 25°C on potato dextrose agar. The number of bacteria was measured per gram of fresh soil (Table I).

**Table I** Number of Bacteria in Garden Soil (Number/g)

Bacteria	10–20 cm Depth	40–60 cm Depth
Viable cell	$7.6 \times 10^6$	$1.9 \times 10^6$
Anaerobes	$4.8 \times 10^5$	$2.3 \times 10^6$
Clostridia	$2.5 \times 10^5$	$3.2 \times 10^5$
Eumycetes	$2.2 \times 10^5$	$4.7 \times 10^4$

**Table II Identification of Bacteria in Garden Soil**

10–20 cm Depth	40–60 cm Depth
<b>Molds</b>	
<i>Aspergillus niger</i>	<i>Aspergillus niger</i>
<i>Fusarium</i> sp.	<i>Penicillium</i> sp.
<i>Penicillium</i> sp.	
<i>Candida</i> sp.	
<b>Bacteria</b>	
<i>Clostridium</i> sp.	<i>Clostridium</i> sp.
<i>Bacillus cereus</i>	<i>Bacillus cereus</i>
Subsp. <i>mycooides</i>	Subsp. <i>mycooides</i>
<i>Bacillus subtilis</i>	

Identification was performed according to *Bergey's Manual*. The results are shown in Table II. The number of aerobes seemed to decrease with the depth, while the number of anaerobes increased with the depth. The total number of bacteria per unit weight of the soil is roughly the same as that of compost.<sup>7</sup> It was made clear that the LDPE films were discarded with kitchen dust. Hence, the soil was kept biologically active for a long time. The kind of identified bacteria and eumycetes were less for the soil collected from 50 cm depth, which indicates the bioactivity of the soil decreases on the whole with increasing depth.

The method of chemical analysis is summarized in Table III and the results are shown in Table IV. The water content was lower, while the content of inorganics was somewhat higher for the soil from 10 cm depth than from 50 cm depth. Each soil was neutral and seemed to be very appropriate for the activity of bacteria, as is shown by the pH values.

## RESULTS AND DISCUSSION

### Appearance of Samples, Observation by Phase Contrast Microscope, and Scanning Electron Microscopy

PS, PVC, and UF which were collected around 10 cm depth from the surface visually showed no rough portions (Figs. 1–3). We examined the color and the transparency of the original sample and the sample of which the surface was deleted. No difference was observed. Any small hole and hyphae were not observed by phase contrast microscopy and by scanning electron microscopy (SEM).

**Table III Methods of Chemical Analysis**

Item	Testing Method and Standard
Active acidity: pH (H <sub>2</sub> O)	Standard test for pH of soils <sup>a</sup>
Latent acidity: pH (KCl)	
Moisture content	Drying at 110°C <sup>b</sup>
Organic compound	Ignition loss in electric furnace at 700°C <sup>a</sup>
Inorganic compound	Ignition residue <sup>a</sup>

<sup>a</sup> Standard of soil engineering society.

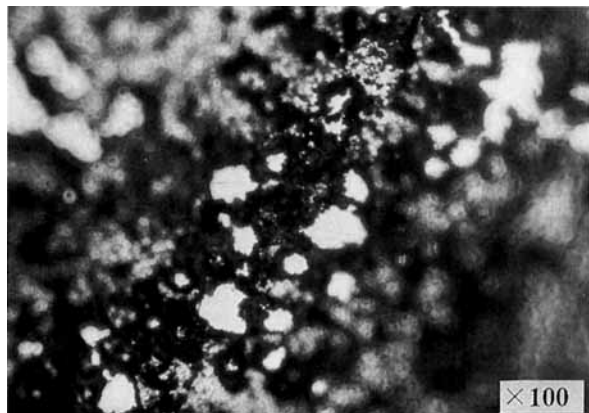
<sup>b</sup> Weight percent of water to dried soil according to JIS (Japanese Industrial Standard) A 1023.

On the other hand, all the LDPE films were partly whitened irrespective of the depth from the surface. Moreover, the films which were buried near the surface showed many small holes and part of the film lost its shape. Although the samples collected from 40–60 cm depth from the surface were also whitened, the degree of whitening was evidently small as compared with the films, which were collected from about 10 cm depth. Figure 4 shows the appearance of small LDPE fragments (sample 3). Both sides of these fragments were in contact with soil and so severely degraded that we could not recognize the original form of the sample. Figure 5 (sample 2) is a triangular film bag for juice. The degradation of the inner surface of the bags was not so severe. We could even recognize a gloss on part of the inner surface except for the severely degraded parts where the holes went through the film. We also found long strips of thin LDPE film which were tied together (Fig. 6, sample 3). These samples are very important because a part of the film was directly in contact with the soil, while the other part was not. Figure 7 shows the appearance of an opened film. As shown here, the part that was not in contact with soil was

**Table IV Chemical Analysis of Garden Soil**

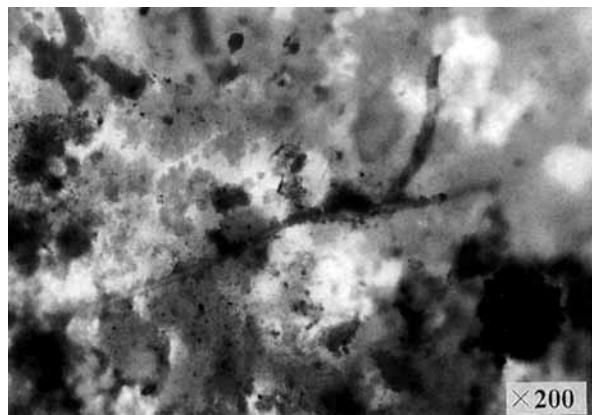
Item	10–20 cm Depth	40–60 cm Depth
pH(H <sub>2</sub> O)	7.4	7.5
pH(KCl)	5.7	5.9
Moisture content, %	34.0	37.9
Water content, % <sup>a</sup>	25.4	27.5
Organic compound, %	6.1	8.1
Inorganic compound, %	68.5	64.4

<sup>a</sup> Weight percent of water to wet soil.

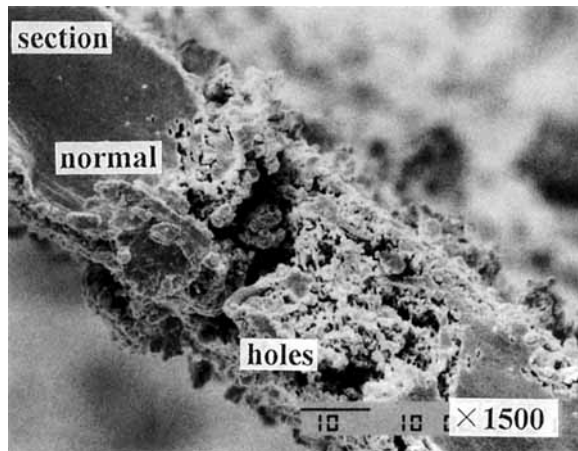


**Figure 8** Observation of small holes in whitened part by phase contrast microscope.

transparent. On the other hand, the part of the film which was directly in contact with soil was whitened and severely degraded. The observation by a phase contrast microscope showed that a lot of holes ranging from 20 to 200 nm of diameter were passing through the film (Fig. 8). Besides, we could see a number of hyphae as shown in Figure 9. The section of the whitened part consists of a lot of holes with a honeycomb-like structure (Figs. 10–12). Figure 13 is very interesting. It looks like the replicas of filamentous fungi. These long wormlike ditches may be formed by the bacteria which is directly in contact with LDPE, and the enzymatic metabolic action of the body dissolves the polymer in the shape of the bacteria. Such ditches are frequently observed for the highly biodegradable plastics such as polyhydroxybutyrate (PHB). We could not identify the bacteria, but the ditches were considered to be formed by a kind of filamentous fungi from the shape. This is probably the first photograph that



**Figure 9** Observation of hyphae on LDPE by phase contrast microscope.

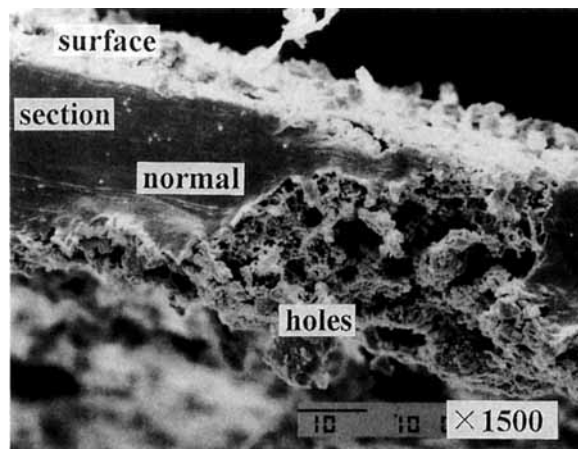


**Figure 10** SEM micrograph of severely degraded part of film section.

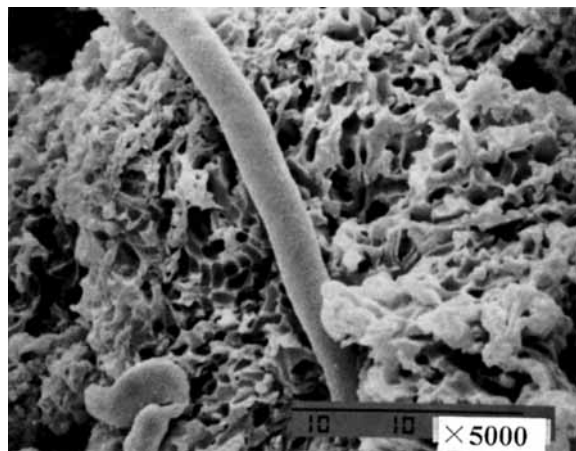
observes direct evidence of the biodegradation of high-molecular-weight LDPE.

#### Analysis of Degradation by Means of Fourier Transform Infrared Microscopy and Differential Scanning Calorimetry

As has been mentioned above, it was recognized that PS, UF, and PVC visually have not degraded. In order to detect evidence of biodegradation at the molecular level, measurement by Fourier transform infrared (FTIR) microscopy using the surface reflectance method was carried out. Spectra were taken by a Bio-Rad DIGIRAB FTS-60, IR microscope UMA-300A. Scans were repeated 256 times. The spectra of the surface of the PS cup were almost the same as those of the standard PS sample. Moreover, the differential spectrum of the surface, which was



**Figure 11** SEM micrograph of small holes almost penetrating film section.



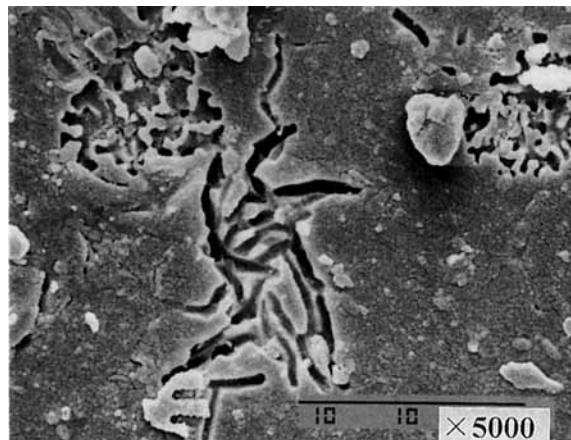
**Figure 12** SEM micrograph of hyphae grown on film surface.

directly in contact with soil, was recorded with reference to the sample which was cut from the inner part. Although it has been reported that oligomeric PS does biodegrade,<sup>1,8</sup> we could not find any evidence of the difference in the spectra between the surface and inner part for the PS sample. Similarly, the spectra of the surface of the UF jar and inner part were almost the same. PVC seems to be difficult to biodegrade, the plasticizer included in PVC compounds may possibly become the nutrition source and accelerate the degradation of PVC. We compared the FTIR spectrum of the extreme surface of the PVC samples with that of the inner surface where the extreme surface was deleted. The intensity of the carboxyl band of phthalic acid esters at  $1720\text{ cm}^{-1}$  of the former was a little bit smaller than that of the latter. However, it is also probable that the phthalic acid ester was volatilized. Thus we could not find any evidence of degradation also for the PVC sample.

It was reported that the oxidative degradation of LDPE proceeds much faster in bioactive soil.<sup>9</sup> We found that the characteristic feature of the biodegradation of LDPE is the whitening, as has been stated before. Such whitening was hardly observed for LDPE degraded under thermooxidative or photooxidative conditions.

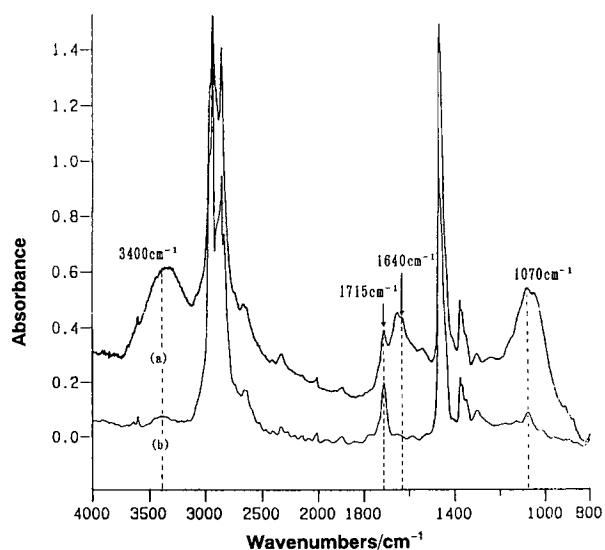
#### FTIR Analysis

The degradation of LDPE was analyzed by FTIR analysis using characteristic bands ranging from  $1600$  to  $1750\text{ cm}^{-1}$ . We found two main characteristic bands for the whitened part of degraded LDPE which were not observed for undegraded samples. The one is the band observed in the vicinity of  $1715\text{ cm}^{-1}$



**Figure 13** SEM micrograph of wormlike ditches on film surface.

$\text{cm}^{-1}$  and could be assigned to  $\text{C}=\text{O}$  groups formed in the course of degradation. The other quite unexpected broad band appeared in the vicinity of  $1640\text{ cm}^{-1}$ . This may be assigned to unconjugated  $\text{C}=\text{C}$  band which was also indicated by Albertsson et al.<sup>10</sup> and considered to be characteristic of biodegradation. In fact, there was no indication of the presence of unconjugated  $\text{C}=\text{C}$  band for the LDPE films degraded under thermooxidative condition. It is very interesting that the clear part of the folded film did not show any evidence of  $\text{C}=\text{C}$  bands as shown in Figure 14. The total outlook of the spectrum was quite similar to that of the degraded film under the thermooxidative condition. Hence it seems that the biodegradation of LDPE film proceeds only when



**Figure 14** FTIR surface reflectance spectra of tied film: (a) whitened part; (b) clear part.

the film is directly in contact with bioactive soil. The hydroperoxide band in the vicinity of  $3600\text{ cm}^{-1}$  was observed both for whitened and clear parts, while the intensity of the broad hydroxy band in the vicinity of  $3400\text{ cm}^{-1}$  was stronger for the whitened part. The relative intensities of the carbonyl band at  $1715\text{ cm}^{-1}$  and the  $\text{C}=\text{C}$  band at  $1640\text{ cm}^{-1}$  to that of methylene band at  $1470\text{ cm}^{-1}$  are summarized in Table V.

### Initial Oxidation Temperature by Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) traces of LDPE show a clear upturn around  $200^\circ\text{C}$  under oxidation atmosphere. This upturn is due to the start of the oxidation of LDPE. We defined the temperature at which the first upturn occurs as the initial oxidation temperature (IOT). It has been recognized that the IOT of thermooxidized LDPE decreases with increasing degree of oxidation. The IOT of buried LDPE is summarized in Table VI. As can be shown in the table, the IOT of the clear part of the degraded sample is about  $15^\circ\text{C}$  lower than that of untreated LDPE. This indicates that considerable degradation occurs also in the clear part. The IOT of the whitened part is still lower than that of the clear part. Thus marked oxidative degradation of LDPE in contact with soil is evident.

### Reason for the Whitening

As mentioned above, the remarkable whitening occurs for the highly degraded part of the film. A pos-

**Table V** Relative Intensity of Carbonyl and  $\text{C}=\text{C}$  Bands by FTIR Microscope

Sample	$1715\text{ cm}^{-1}$	$1640\text{ cm}^{-1}$
No. 1 (rag)		
Inside	0.05	0.108
Outside	0.08	0.071
No. 2 (juice bag)		
Inside	0.15	0.064
Outside	0.15	0.069
No. 3 (tied film), clear part		
Inside	0.09	0.004
Outside	0.13	0.022
No. 3 (tied film), whitened part		
Inside	0.09	0.172
Outside	0.08	0.085

Note: Relative intensity was calculated against intensity of methylene band at  $1470\text{ cm}^{-1}$ .

**Table VI** Initial Oxidation Temperature Determined by DSC

Sample	Initial Oxidation Temp. ( $^\circ\text{C}$ )
Control LDPE	213.5
No. 2 (juice bag)	
Clear part	196.0
Whitened part	189.0
No. 3 (folded film)	
Clear part	201.5
Whitened part	189.0

sible reason for the whitening is the increase of the degree of crystallization. Thus we examined the crystallinity of the clear and whitened parts of the folded LDPE film using an X-ray diffractometer (Philips PW-1710-1729). The X-ray diffraction profiles for clear and whitened parts were similar, but the half width of the most intense peak was larger for the whitened part ( $0.55^\circ$ ) than for the clear part ( $0.48^\circ$ ). This indicates that the crystallinity is higher for the clear part, which is contrary to the prediction. The X-ray results show that the whitening is not caused by the change of the crystallinity but is probably brought about by erosion due to the biodegradation.

### CONCLUDING REMARKS

We have examined the biodegradation of several polymers buried under soil for over 32 years. We could not find any evidence of biodegradation for PS, PVC, and UF resin. For LDPE, however, remarkable whitening of the film which was directly in contact with soil was observed. A lot of small holes which are passing through the film was observed around the whitened part. The degradation was more remarkable for samples which were buried in shallow places where the activity of aerobes is high. We could find many hyphae on the whitened part of the film. Moreover, we could also find long wormlike ditches which are possibly formed by the metabolic action of filamentous fungi. The analysis by FTIR microscopy of the whitened part showed that a characteristic band appeared in the vicinity of  $1640\text{ cm}^{-1}$  which was assigned to the  $\text{C}=\text{C}$  bond. We considered that this band was brought about by biodegradation. On the other hand, this band was missing for clear parts of the film, and we could observe only the carbonyl band which is characteristic

of the usual thermooxidative degradation. The results show that high-molecular-weight polyethylene can really biodegrade under bioactive circumstances if the test period is long enough.

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