Oxidative Degradation and Molecular Weight Change of LDPE Buried under Bioactive Soil for 32–37 Years

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Received 18 September 1996; accepted 30 December 1996

ABSTRACT: The molecular weight reduction of low-density polyethylene (LDPE) buried under bioactive soil for 32–37 years was examined by GPC. Microscope IR spectra of the surface of the degraded sample showed the characteristic feature of biodegradation, while the inner part of the sample was almost unchanged. The number average molecular weight (M_n) of the surface was reduced to almost one-half of the inner part. Moreover, a low-molecular-weight component around a molecular weight of 10^3 was recognized for degraded samples. SEM observation suggested that the formation of the low-molecular-weight components is the result of erosion due to enzymatic reaction. The results give evidence for the biodegradation of high-molecular-weight LDPE. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1643–1659, 1998

INTRODUCTION

In a previous article, we determined that notable oxidative degradation of LDPE film buried in soil for 32–37 years was accompanied by molecular weight reduction.[1] Degradation of the LDPE was discernible at whitened parts that were kept directly in contact with soil. This phenomenon suggests that bioactivities in soil participate in the degradation. The measurement of molecular weight and its distribution in samples taken from both whitened parts and somewhat less degraded clear parts in the film was carried out. Although there were large differences in the degradation between the two parts, significant differences in molecular weight between them were not found. Assuming that the degradation of LDPE under bioactive influences is caused not only by exogenous decomposition at terminals of the molecular chains but also by decomposition of hydroperoxides formed by an endogenous mechanism along the molecular chains as is generally accepted, the above result is difficult to comprehend. If the decomposition takes place along the molecular chains, a large decrease of molecular weight caused by slight degradation should be found. No investigation of the biodegradation of PE in the past has proved that the molecular weight was affected by the degree of degradation. Investigations in the past have resulted in hypotheses to explain that biodegradation only takes place by an exogenous mechanism and hence minor molecular weight changes.

The number average molecular weight of the LDPE films measured in experiments published earlier was about 1.2×10^4 after long-term oxidative degradation. Judging from the thickness and shape of the films measured, we estimated that the LDPE films were formed by the inflation process. However, the molecular weight mentioned above is far less than 2×10^4, that of normal

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Journal of Applied Polymer Science, Vol. 70, 1643–1659 (1998)
 CCC 0021-8995/98/091643-06

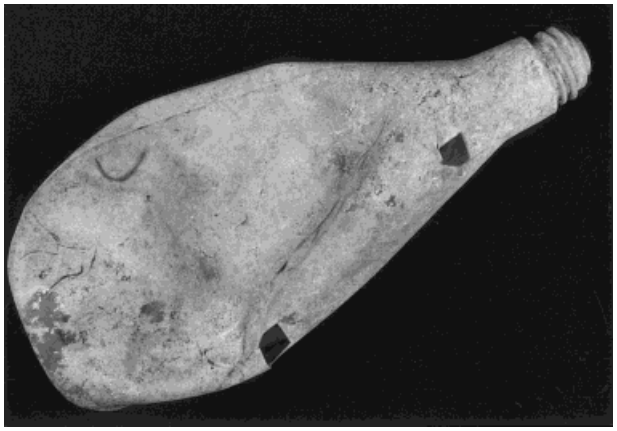

Figure 1 Appearance of LDPE mayonnaise bottle.

LDPE film made by the inflation process. Consequently, it is reasonable to accept that the lack of difference in molecular weights between the whitened parts and the clear parts is not because of less oxidative degradation. Judging from their molecular weight, the two parts were degraded to the same level. The samples of LDPE film used in the previous study were so thin that the oxidative degradation took place throughout their thickness. This phenomenon was proved by analysis. Fourier transform infrared (FTIR) measurement was applied to an outer surface of the film which was in direct contact with soil and also to an inner surface of the film which did not contact soil. From the results, we found that there were minor differences in the degradation between both surfaces. To evaluate the change of the molecular weight in the course of the degradation, it is necessary to measure the degradation throughout the depth of thicker samples. A mayonnaise LDPE bottle, perhaps made by blow molding, was fortunately excavated from the same place from which the samples examined earlier and described in the previous article were excavated (Fig. 1).

As described in the previous article, it is known that these waste plastics were buried in bioactive, rather shallow soil under enough aerobic conditions for 32–37 years. We have examined thick parts of the bottle to estimate biodegradation throughout the thickness of the LDPE samples.

EXPERIMENTAL

Samples

Qualitative analysis of the polymer of the mayonnaise bottle was executed by means of PGC, FTIR, and differential scanning calorimetry (DSC). The spectral pattern with FTIR and the melting point with DSC and the PGC chromatogram well conformed to the results of analysis of F31N (Nippon Oil Co., Ltd.) used as standard LDPE. The samples were consequently accepted as LDPE. As shown at Figure 2, samples (A), (B), and (C) for measurement were cut out from a shoulder part of the mayonnaise bottle. Sample (A) was taken by carefully scratching from the whitened shoulder part of the bottle with a spurtle because only the surface is used to degrade and the inner part is used to stay undegraded in case of enzymatic degradation. After sample (A) was taken out as described above, sample (B) with a thickness of 15–20 μm was cut out from the surface with a knife. Sample (C) was taken from the center part of the thickness. Sample (C) was not whitened but transparent.

Measurement

We made measurement of the molecular weight and its distribution by GPC, with a Waters GPC-150C, using *o*-dichlorobenzene as a solvent at a temperature of 140°C. FTIR microscopy analysis was made with Bio-Rad DIGIBLAB, FTS-60, and its supplementary Infrared Ray microscope UMA-

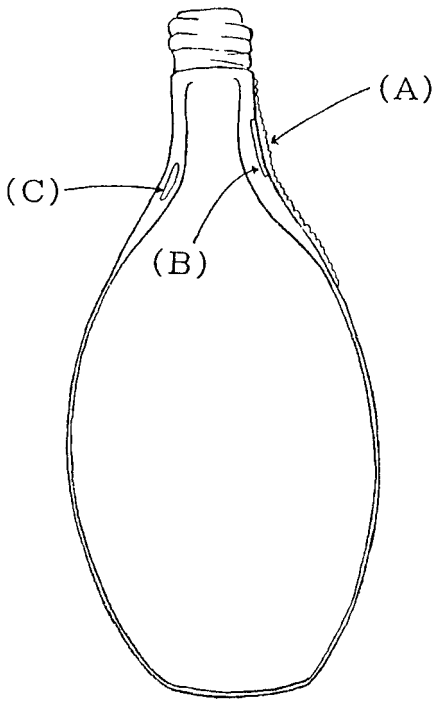

Figure 2 Sampling of mayonnaise bottle for molecular weight measurements. (A) Whitened part on the extreme surface, (B) thin section just under the surface, (C) central part.

Table I Molecular Weight Measurement of Samples (A), (B), and (C)

Sample	Number Averaged M_n	Weight Averaged M_w	Q Value M_n/M_w
(A)	1.25×10^4	1.03×10^5	8.20
(B)	1.29×10^4	1.20×10^5	9.28
(C)	2.05×10^4	1.45×10^5	7.10

300A, by a surface reflectance method (scanning times, 256). Samples (B) and (C) were measured with the same conditions as for sample (A), by a surface reflectance method, making the surfaces into a front face (being closer to soil) and a back face (being farther from soil).

RESULTS AND DISCUSSION

Molecular Weight and Its Distribution

Number average molecular weight (M_n), weight average molecular weight (M_w), and Q values as an index of the molecular weight distribution are listed in Table I. The molecular weight distribution curves by GPC are shown in Figure 3.

Regarding the molecular weight of sample (A), taken from right under the surface, as presented at Table I, it was found that M_n decreased to about one-half of that of sample (C), extracted from the center part of the thickness, and that M_w decreased to about two-thirds. A decrease of the molecular weight of high-molecular-weight PE by degradation under the bioactive circumstances at room temperature has not been observed directly in the past; this investigation is the first reported case. The molecular weight of sample (B), extracted from right under the surface, was almost the same as that of sample (A). Judging from the molecular weight distribution curves, it is also recognized that a low-molecular-weight component of (A) and (B) with their molecular weight of about 10^3 considerably increased, compared with that of (C). By contrast, however, it is found that a high-molecular-weight component of molecular weight of approximately 10^6, found in (C), is decreased in (A) and (B) while approaching the surface. So, we consider that oxidative degradation of thick film samples like these under the bioactive soil burial conditions occurs within the limited thin layers that are closer to the surface.

Meanwhile, the molecular weight of sample (C), which was extracted from the center of the thickness of the samples, was nearly the same as that of LDPE, obtained generally by a blow molding process. Thus, think that because (C) is located at a 1-mm depth from the front (or back) surface, (C) could have kept its original molecular weight and its distribution without undergoing oxidative degradation and biodegradation under the conditions of burial in soil for more than 30 years. It is therefore proposed that sample (C) can be used as the standard undegraded sample.

It is interesting that the degradation seems to be controlled in terms of diffusion rate and is limited to areas near the surface, despite more than 30 years' exposure in soil. The rate of the oxidative degradation of LDPE in soil is extremely slow, although it is faster than that in air. We think that since a diffusion coefficient of oxygen in LDPE is not that small as compared with the rate

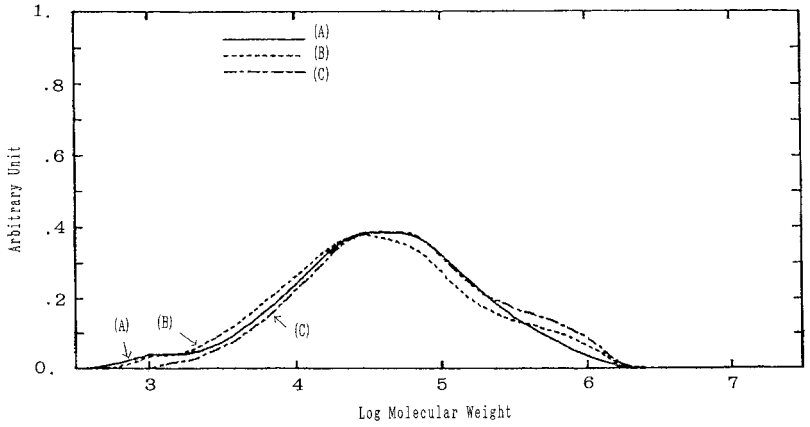

Figure 3 GPC molecular weight distribution of samples (A), (B), and (C). (A) Whitened part on the extreme surface, (B) thin section just under the surface, (C) central part.

of oxidation, the apparent diffusion-controlled degradation is due to an unusual reaction occurring at the surface layer in contact with soil. Examples of several reactions like these, for example, the catalytic decomposition of hydroperoxide by metal ions in soil and the oxidative degradation of LDPE itself promoted by microbial activities, are given as described in previous articles.[2,3]

Almost no investigation has been made to estimate the molecular weight change under conditions of normal oxidative degradation, conditions not intentionally made at high temperature, that is, no heat aging, but almost natural aging for a long time. Ohtake et al.[4] surveyed the molecular weight changes with GPC under heat treatment at 50°C for 400 days and at 100°C for 400 days. At 50°C, the oxidative degradation was developed similar to that of natural aging. From these results, we noted that M_w decreased but M_n did not change and that the spread of the molecular weight distribution became narrow. It is, however, claimed that in the case of heat treatment at 100°C, the decrease of M_n and gelling were observed at the same time. There are obvious differences between the above result obtained through Iyota's research and the result of the molecular weight change obtained through our investigation. That is, in the degradation which seems to be caused by bioactivities, lowering the molecular weight is unique, and the molecular weight distribution spreads to the low molecule side with lowering of M_n. This contrast with the molecular weight distribution becoming narrow without lowering of M_n, in the case of usual oxidation, except in the case of high-temperature treatment.

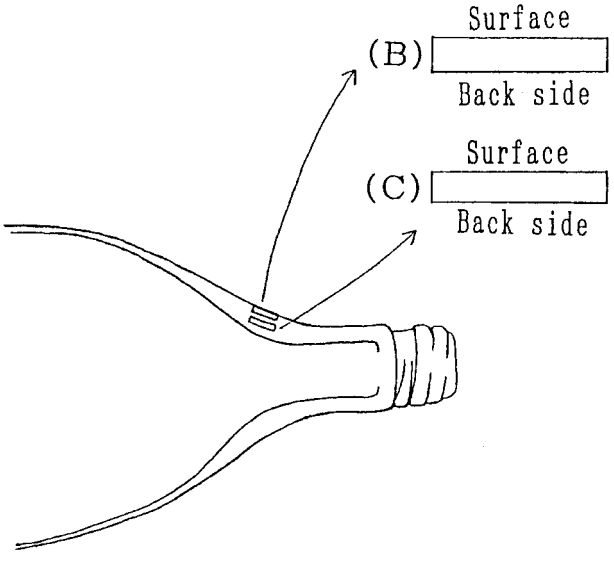

Figure 4 Measurement of FTIR. Samples (B) and (C) are the same as indicated in Figure 2.

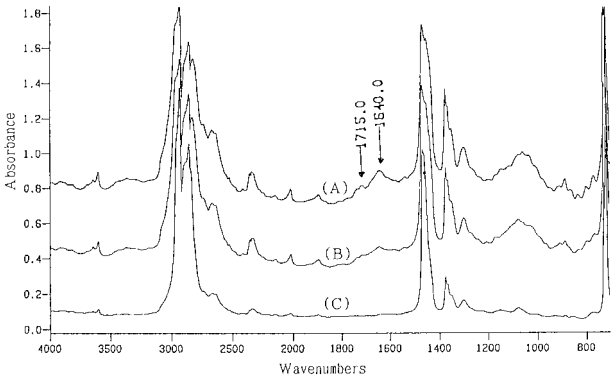

Figure 5 FTIR microscopy spectra for samples (A), (B), and (C).

Measurement of Degradation by the FTIR Microscope Reflectance Method

FTIR measurements of sample (A), which were the same as with the samples applied to GPC measurement, were executed by the microscope reflectance method. The back side of sample (B) was also measured (Fig. 4).

Microscope FTIR spectra for samples (A), (B), and (C) are presented in Figure 5. The intensities of absorbance of carbonyl groups, C=C double bond, and other groups, which are displayed in Table II, were obtained by being related to that of C—H out-of-plane deformation. These characteristic absorbances are not seen in sample (C). The spectral pattern is quite similar to that of undegraded commercial LDPE; hence, we have discovered that the LDPE bottle was hardly degraded despite its burial in soil for more than 30 years, consistent with the results of the abovementioned GPC measurement.

The absorption rates of hydroperoxide and hydroxyl groups appear near 3,600 and 3,400 cm^{-1} and are seen in the spectra of samples (A) and (B). In particular, another characteristic feature is the strong absorbance intensity of the C=C double bond in the range of 1,640–1,650 cm^{-1}, which is a phenomenon peculiar to biodegradation.[1] It is also noted that the absorption rates of carbonyl groups and the C=C double bond were decreased at the back surface of sample (B), compared with the front. As a result of this information, it can be considered that the occurrence of the oxidative degradation of thick LDPE samples, even if buried in soil for more than 30 years, is limited to the extreme surface and is almost never

Table II Characteristic Absorption Bands Obtained by FTIR Microscopy

Sample	1,715 cm^{-1}/ 1,470 cm^{-1} Absorbance Ratio (Carboxylic Acid)	1,640 cm^{-1}/ 1,470 cm^{-1} Absorbance Ratio (—C=C—)	1,742 cm^{-1}/ 1,470 cm^{-1} Absorbance Ratio (Ester)	1,721 cm^{-1}/ 1,470 cm^{-1} Absorbance Ratio (Ketone)	3,600 cm^{-1} Absorbance (OOH)	3,400 cm^{-1} Absorbance (OH)
(A)	0.0545	0.1199	0.0468	0.0609	0.0934	0.0294
(A)	0.0323	0.0529	0.0548	0.0254	0.0739	0.0254
(B) Surface	0.0322	0.0531	0.0275	0.0323	0.0779	0.0193
(B) Back side	0.0299	0.0428	0.0234	0.0277	0.0698	0.0195
(C) Surface	0.0015	0.0058	0.0046	0.0021	0.0520	0.0089
(C) Back side	0.0018	0.0051	0.0040	0.0090	0.0511	0.0070

Samples (A)–(B) correspond to those shown in Figure 3. The spectrum of sample (A) was taken from two different parts.

developed on the inside. It is also significant that the progress of degradation is slow from the surface to the inside. However, similar functional groups formed by the oxidization are seen, regardless of their depth.

As stated in a previous article,[2] we think that long-term oxidative degradation under soil burial conditions must not be developed with a simple degradation mechanism, but must be developed with a complex degradation mechanism composed of several factors such as normal oxidization, effects of moisture, and metal ions in soil and biodegradation. We were not able to find evidence to show that bioactivities engaged in the oxidative degradation, in the case where the LDPE film was thin and did not contact soil. However, if samples are thick, like those used in this investigation, oxidized products, which characterize the biodegradation, will be generated, whether or not they are kept in direct contact with soil, like the back surface of sample (B). This points to degradation, in which microbes participate, developing from the surface to the inside of the film; the rate of degradation progressing to the inside is determined by the diffusion rate of metabolites from microbes, not by that of oxygen, water, and metal ions.

Observation of the Film from Which *n*-Hexane Was Extracted

We hypothesize that since the decrease of the molecular weight is by an active enzymatic reaction at the ends of microcavities at the film surface, which seem to be created by enzymatic erosion and do not penetrate throughout the film thickness, the lower molecular weight polymers must thereby be dissolved by *n*-hexane extraction. If so, it can be considered that the formation of such microcavities in the LDPE is obviously caused by the decrease of the molecular weight. We there-

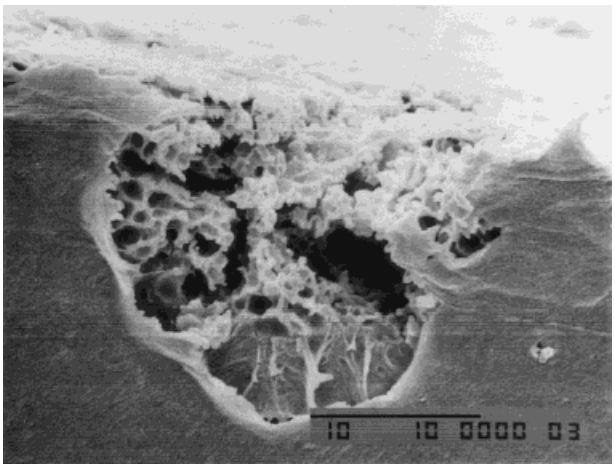

Figure 6 LDPE film section, before extraction (×3,500).

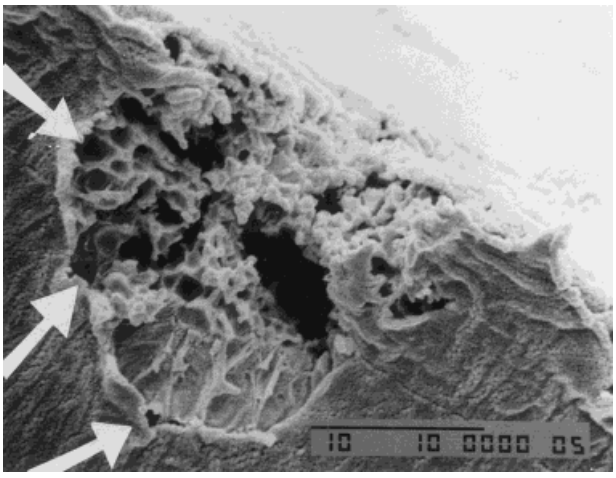

Figure 7 LDPE film section, after extraction by *n*-hexane, (×3,500).

fore made an observation with by scanning electron microscopy of the said parts before and after extracting the *n*-hexane. Figure 6 (before extracting) and Figure 7 (after extracting), which present the same parts, are the results of the observation. Also, Figures 8 and 9 exhibit the conditions of the before and the after as well. The surface condition of the wall's cross-section after extraction with the *n*-hexane looks somewhat rougher. We consider that these phenomena resulted from swelling with *n*-hexane and drying. We postulate that polymer was removed from the inner surfaces of the walls of the microcavities', after extraction (arrows in Figures 7 and 9). We, therefore, think that the decrease of the molecular weight caused by the decay and the decomposition under the influence of the bioactivities has resulted in forming such microcavities.

CONCLUSIONS

We investigated the molecular weight and its distribution in LDPE samples that were produced by blow molding and buried in soil for more than 30 years. The tailing of the GPC peaks toward the low-molecular-weight side and the decrease of M_n to half of the usual value, compared with polymer from an area which was not affected by the oxidative degradation, indicate a difference from the normal oxidative degradation. The appearance of microcavity cross-sections in the LDPE film suggests that they were created by erosion caused by enzymatic reactions. Extraction with *n*-hexane suggested that erosion produced a low-molecular-weight polymer.

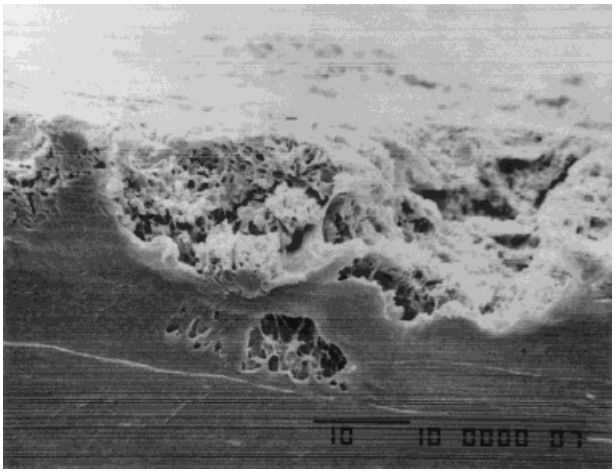

Figure 8 LDPE film section, before extraction (×2,000).

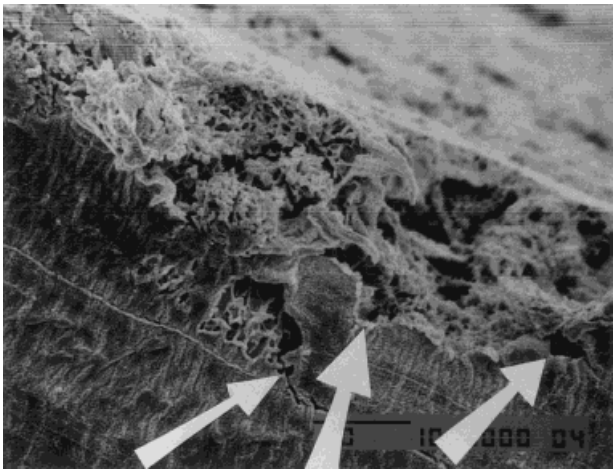

Figure 9 LDPE film section, after extraction by *n*-hexane (×2,000).

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