

## Depth Profiling Analysis of Functional Groups in Outdoor-Exposed Polyethylene Using Derivatization-Electron Probe X-Ray Microanalysis

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**ABSTRACT:** A new analytical method referred to as “Derivatization-Electron Probe X-Ray Microanalysis (XMA)” has been developed to determine the distribution of 0.1% order functional groups in polymers with micron level lateral resolution. Depth profiles of the functional groups in the polyethylene (PE) degraded by the outdoor-exposure were determined using this method. The results suggested that the PE degrades from the surface and the backface due to the oxidation during the outdoor-exposure, and the rain extracts the oxidation products generated near the surface. Also, it was confirmed that the load by water was indispensable for the accelerated weathering test. The sensitivity of the derivatization-XMA was approximately 2–6 times higher than that of micro-IR. Through this research, the utility of the derivatization-XMA method for studying the degradation mechanism and characterizing polymers was confirmed.

**KEY WORDS** Depth Profiling / Functional Group / Polyethylene / Outdoor-Exposure / Derivatization / Chemical Modification / Electron Probe X-Ray Microanalysis (XMA) /

It is well known that polymers degrade under environmental conditions being affected by light, heat, etc., thus losing their properties. Therefore, it is important to study the degradation mechanism of the polymers and also to develop a method for estimating the degradation degree of the polymers. In order to estimate their degradation, both chemical and physical points of view are definitely necessary. From the chemical point of view, we are very much concerned with the changes in the composition and functional groups that occur during the degradation, especially on the surface and within the sample.

Since infrared absorption spectroscopy (IR) provides very valuable information about the chemical structure and micro measurement (micro-IR) is available, the use of IR for the depth profiling of the compositions and the functional groups is increasing.<sup>1–3</sup> Especially, for the depth profiling, a depth resolution of micron order was achieved. It has been used for the estimation of the degraded polymers, etc.<sup>4</sup> However, the measurement of any change of less than several percent of the components is difficult using IR.

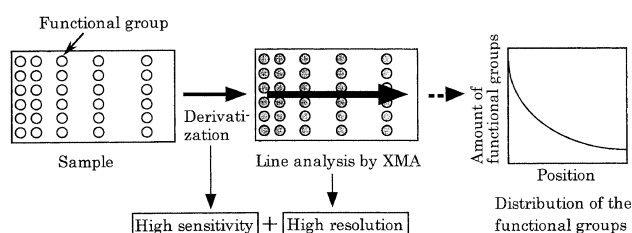
Therefore, a newer analysis method to measure the distribution of small amounts of the functional groups generated in the degraded polymers with a lateral resolution of micron order using generally available equipment was searched.<sup>5</sup> An effective microanalysis “derivatization- electron probe X-Ray microanalysis (XMA)” combining chemical derivatization for the detection sensitivity and XMA was then developed. This

method is useful for estimating the degraded polymers and studying of the degradation mechanism of the polymers.

An outline of the derivatization-XMA is shown in Figure 1. This method first derivatizes the functional groups in a polymer using a derivatizing reagent with an indicator element highly sensitive to XMA and, moreover, with high selectivity to the functional group, and then measures the distribution of the indicator element, thus obtaining the distribution of the original functional groups. It was designed to increase the sensitivity and the lateral resolution using the chemical derivatization and XMA, respectively.

Polyethylene (PE) is a cheap and common plastic. Its physical properties are excellent, and it is thus widely used. The degradation mechanism of the PE has been studied in detail.<sup>6–8</sup> It is known that during the oxidation degradation, carbonyl groups, carboxyl groups and hydroxyl groups are generated in the PE.

In this study, the depth profiles of these functional



**Figure 1.** Scheme for the derivatization-XMA.

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groups in the PE degraded by the outdoor-exposure were determined using this method.

## EXPERIMENTAL

### Outdoor-Exposure of the PE

The Polyethylene (PE) (Asahi Kasei Co., Ltd., Santec J320) was outdoor-exposed based on JIS Z 2381 (inclination angle: 45°) in Nagakute (Aichi, Japan) from Sept. 1995 to Mar. 1997. The PE was molded into a test piece based on JIS K 7113 (1 type dumbbell, 175 × 20 mm, 3 mm thick).

### Line Analysis Using XMA

The PE degraded by the outdoor-exposure was cut perpendicular with a microtome. The cut surface was line analyzed using XMA in the depth direction after being derivatized under optimal conditions. For the line analysis, a Shimadzu EPM-810Q was used as the XMA equipment, and the beam diameter, the acceleration voltage, the sample electric current and the scan speed were set to 1 μm, 20 kV, 20 nA, and 50 μm min<sup>-1</sup>, respectively.

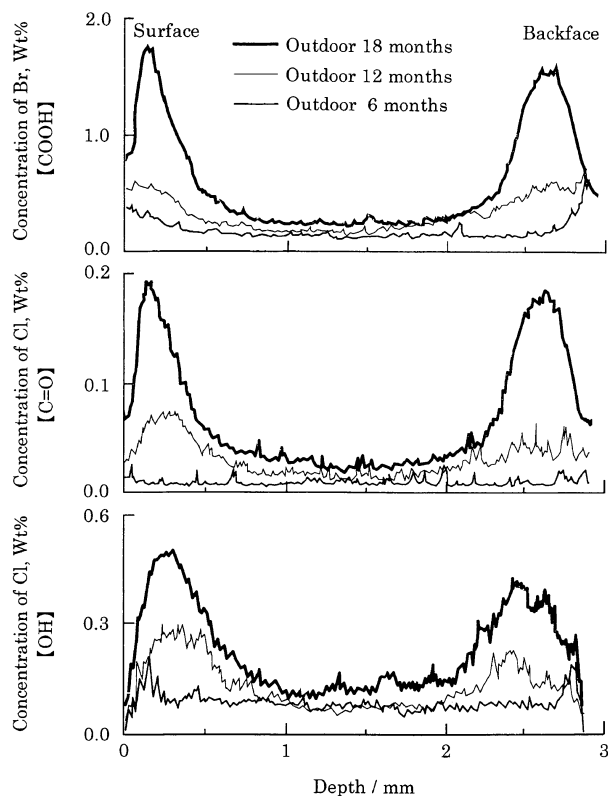
### Derivatization of Functional Groups

The carboxyl groups, the carbonyl groups and the hydroxyl groups were derivatized as follows.

**Derivatization of Carboxyl Groups.** 2,2,2-Tribromo ethanol (TBE, Aldrich Chemicals Co., Ltd.), pyridine (Wako Pure Chemical Industries, Ltd.) and dicyclohexylcarbodiimide (DCC, Aldrich Chemicals Co., Ltd.) were used as the derivatizing reagent, the reaction catalyst and the dehydrating agent, respectively. The sample was placed in a vial and the reaction solution was poured in it without directly contacting the sample. The reaction solution was as follows. The reagents in the 50 mL vial were TBE (70 mg), pyridine (70 μL), and DCC (50 mg). The vial was then heated at 110°C for 120 min. After the reaction, the sample was vacuum dried overnight at 110°C.

**Derivatization of Carbonyl Groups.** The reaction solution was 2.5% 2,4,6-trichloro phenyl hydrazine (TCPH, Aldrich Chemicals Co., Ltd.) in acetic acid (Wako Pure Chemical Industries, Ltd.). The sample was placed in a vial and the reaction solution was poured in. The vial was then heated at 90°C for 30 min. After the reaction, the sample was dipped in acetic acid for 10 min, then vacuum dried overnight at 25°C.

**Derivatization of Hydroxyl Groups.** The sample was placed in a vial and trichloroacetic anhydride (TCAA, Aldrich Chemicals Co., Ltd.) was poured in it without directly contacting the sample. The amounts of reagent in the 50 mL vial was 50 μL. The vial was then heated



**Figure 2.** Depth profiles of the functional groups in the outdoor-exposed PE obtained using the derivatization-XMA.

at 60°C for 90 min. After the reaction, the sample was vacuum dried overnight at 60°C.

### Line Analysis Using Micro-IR

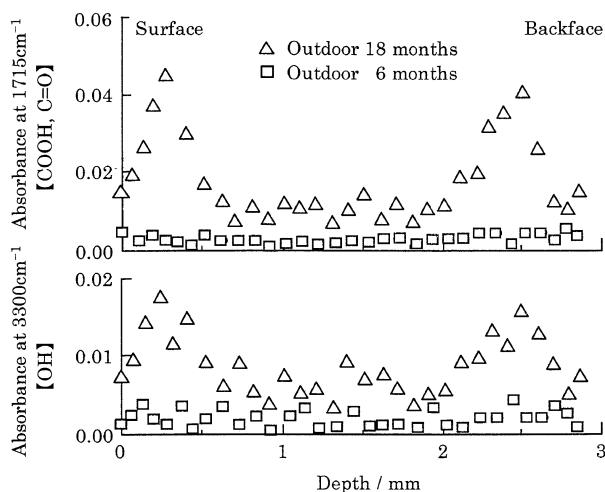
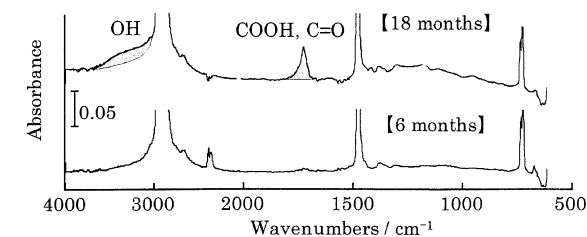
The PE degraded by the outdoor-exposure was cut perpendicular with a microtome. The obtained 1 μm thick film was line analyzed using micro-IR in the depth direction. For the line analysis, a JEOL JIR-100 type Fourier transform infrared spectrometer with a MAU110 type micro-IR unit was used, and the slit size and the spending width were set to 20 μm × 50 μm and 20 μm, respectively.

## RESULTS AND DISCUSSION

### Depth Profiling of Functional Groups in the Outdoor-Exposed PE

The PE was outdoor-exposed for 6 months, 12 months, and 18 months. The depth profiles of the carboxyl groups, the carbonyl groups and the hydroxyl groups in the outdoor-exposed PE were determined using the derivatization-XMA. The obtained depth profiles of the functional groups are shown in Figure 2.

The generation of the carboxyl groups in the PE exposed for 6 months and 12 months is observed on the surface and gradually decreases to *ca.* a 500 μm depth, and then becomes constant. Also, the quantity of the carboxyl groups in the PE exposed for 12 months is



**Figure 3.** IR spectrum of the outdoor-exposed PE at a 200  $\mu\text{m}$  depth (upper) and depth profiles of the oxidation products in the outdoor-exposed PE obtained using micro-IR (lower).

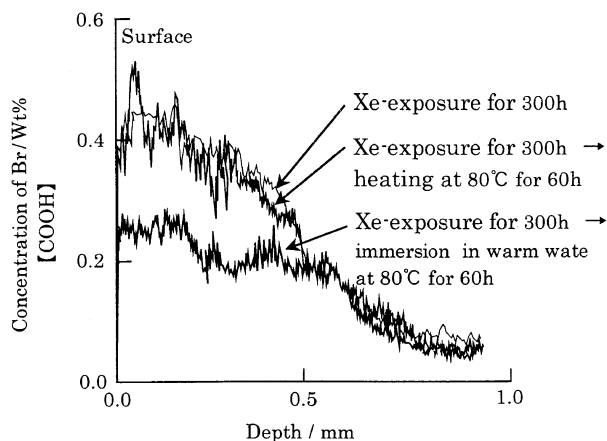
more than that after 6 months. These results suggest that the oxidation occurred during the weathering of the polymer. However, in the PE exposed for 18 months, the quantity of the carboxyl groups decreases near the surface. These profiles clearly indicate that the same phenomenon at the surface occurs on the backface as well. This result suggests that the contribution of oxygen is greater than that of light on the degradation by the outdoor-exposure. These tendencies are also observed in the carbonyl groups and the hydroxyl groups.

Next, the depth profiles of the oxidation products in the same sample were determined using micro-IR. The obtained IR spectra at a 200  $\mu\text{m}$  depth are shown in Figure 3 (upper). The absorption at 1715  $\text{cm}^{-1}$  is due to the carboxyl groups and the carbonyl groups generated in the PE during the degradation. The absorption at 3300  $\text{cm}^{-1}$  is the hydroxyl groups. The depth profiles of the oxidation products using these absorptions are shown in Figure 3 (lower). Since the depth profiles obtained using the derivatization-XMA (Figure 2) agreed well with those obtained using micro-IR (Figure 3 lower), the reliability of the depth profiles obtained using the derivatization-XMA was confirmed.

For the depth profiles obtained from the outdoor-exposure for 6 months, while the function groups were not detected at all using micro-IR, they were detected using the derivatization-XMA. This result definitely in-

**Table I.** The S/N of the derivatization-XMA and micro-IR calculated from the depth profiles of the functional groups in the PE outdoor-exposed for 18 months

Functional group	Derivatization-XMA	Micro-IR
Carboxyl group	24	) 5
Carboxyl group	10	
Hydroxyl group	12	2



**Figure 4.** Depth profiles of the carboxyl groups in the PE degraded by Xenon-exposure, heating after Xenon-exposure, immersion in warm water after Xenon-exposure.

dicates that the sensitivity of the derivatization-XMA is higher than that of micro-IR. The S/N values of both methods, which were calculated from the depth profiles of the functional groups in the PE exposed for 18 months are shown in Table I. These results indicate that the derivatization-XMA sensitivity was approximately 2–6 times higher than that of the micro-IR technique.

#### Depth Profiling of Carboxyl Groups in the Accelerated-Degraded PE

To explain the cause of the phenomenon that the oxidation products decrease near the surface in Figure 2, the following experiment was done. Since the load factors during the outdoor-exposure are mainly light, heat and water (rain), the PE was tested using these load factors under the following conditions: Xenon-exposure for 300 h, heating at 80°C for 60 h after Xenon-exposure for 300 h, and immersion in warm water at 80°C for 60 h after Xenon-exposure for 300 h. The depth profiles of the carboxyl groups in the PE degraded under these conditions were determined using the derivatization-XMA. The obtained depth profiles are shown in Figure 4.

This phenomenon is not observed upon only the xenon-light irradiation, and also not observed upon heating after the xenon-light irradiation. However, it is observed upon immersion in the warm water after the xenon-light irradiation. This result indicates that the water extracts the oxidation products generated on the

surface of the PE. Therefore, it was thought that the decrease in the oxidation products observed on near the surface of the outdoor-exposed PE was caused by the extraction action of rain. Therefore, it was confirmed that the load of the water was indispensable for the accelerated weathering test, which is modeled after the outdoor-exposure.

### CONCLUSIONS

Based on the obtained results, it was found that the PE degrades from the surface and the backface due to the oxidation during the outdoor-exposure, and the rain extracts the oxidation products generated near the surface. Also, it was confirmed that the load by water was indispensable for the accelerated weathering test. The sensitivity of the derivatization-XMA was approximately 2–6 times higher than that of micro-IR. Through this research, the utility of the derivatization-

XMA method for studying the degradation mechanism and characterizing polymers was confirmed.

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