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Chemiluminescence of polyethylene induced by UV irradiation

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Summary

The chemiluminescence(CL) of polyethylene(PE) film induced by UV irradiation was investigated. CL parameter, I_0, which indicates the oxidation rate under UV irradiation was obtained from a kinetic analysis. The I_0 was found to be valuable to evaluate the durability of PE films.

Introduction

As we already reported(1,2), the measurement of chemiluminescence(CL) induced by oxidation reaction of polyolefins under heating in air is useful to evaluate the stability of polyolefins against the thermal oxidative degradation. The degradation or aging of polymers caused by UV irradiation is another serious problem in polymer technologies. For commercial use, especially for the out-door use, it is very important to stabilize polymer materials against UV light. Many studies have been carried out on the structural changes of polyolefins due to UV irradiation, and the durability under UV has been intensively studied(3,4). However, it takes a long period in general to evaluate the durability of polymer materials and the efficiency of stabilizers by use of an out-door exposure test or a sunshine weather-O-meter test. Therefore more efficient method has been required to judge the durability against UV irradiation in shorter time.
Some studies were reported(5,6,7) on the CL of polymer materials induced by UV irradiation, but they did not necessarily correlate the results of CL measurement with the durability of samples. In this work, we have investigated CL of polyethylene films induced by UV irradiation and proposed a CL parameter, which is useful to evaluate the durability against UV light, from a kinetic analysis of CL time-courses after UV irradiation.

Experimental

Materials

Linear low-density polyethylene(LLDPE) and high-pressure low-density polyethylene(HP-LDPE)(Sumikathene-L and Sumikathene, respectively. Sumitomo Chemical Co., Ltd.) were used as samples. They were extruded at 200°C into a blown film of 10μm thickness. Light stabilizer Sanol LS944(concentration in the sam-

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ple: 1000ppm) was used in this work. Sample specimens of $3x3cm^2$ were cut from these films for the CL measurement.

Measurement

CL was measured in air at room temperature by use of a Chemiluminescence Analyzer OX-7-TC(Tohoku Electronic Industry Co., Ltd.) equipped with a micro-computer. UV irradiation was carried out using a low-pressure mercury lamp without any filters(Tohoku Electronic Industry Co., Ltd.). The main wavelength in the spectrum of this mercury lamp is 253.77nm. The CL intensity was counted for every 1 second. The measurement and data analysis were carried out according to the procedure as follows,

i) Sample specimen was irradiated for 60 seconds in air.
ii) UV irradiation was stopped and sample was kept in the dark during decay of fluorescence and phosphorescence from impurities and additives.
iii) CL measurement was started after 30 seconds from the stop of UV irradiation.
iv) CL parameter of I_0, which is described below, was obtained using the least square method from the observed CL time-course.

Out-door exposure test was examined for the same samples and the tensile test of the films after exposure was carried out at 23°C

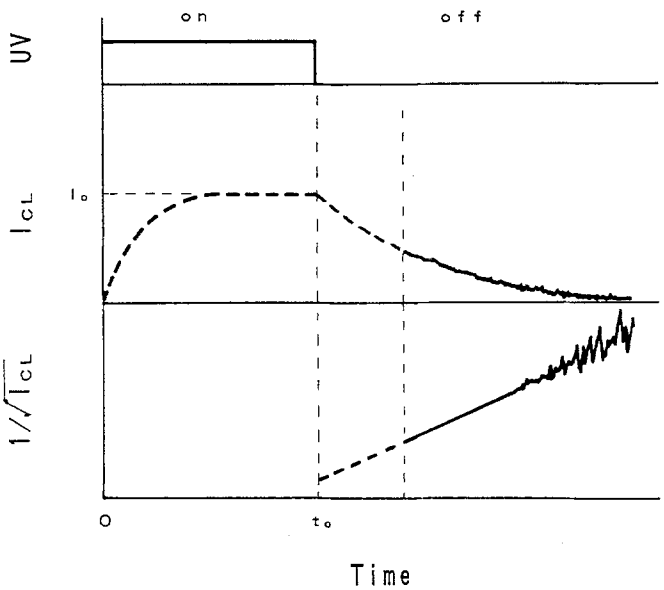

Figure 1 :
Schematic UV irradiation and chemiluminescence time-course for a UV induced chemiluminescence.

Results and discussion

The CL intensity of a polyolefin is proportional to the rate of the bimolecular reaction between peroxy radicals(ROO•) as described in our previous work(1,2),

$$I_{CL} = f \cdot k_b \cdot [ROO\bullet]^2 \quad (1)$$

where I_{CL} is the CL intensity, k_b is the rate constant of the bimolecular reaction, f is the overall efficiency and [ROO•] is the concentration of peroxy radical ROO•. The rate of generation of ROO• by UV irradiation in the presence of oxygen is expressed as follows,

$$d[ROO\bullet]/dt = R_{UV} - k_b \cdot [ROO\bullet]^2 \quad (2)$$

where R_{UV} is the rate of the initiation reaction generating peroxy radical under UV light. From Eqs. (1) and (2), I_{CL} is considered to increase with UV irradiation time and to saturate at some definite value during time-course as shown in Fig. 1(dotted line). Since the left hand of Eq. (2) is equal to zero at this later stage, the following expression holds,

$$I_0 = f \cdot R_{UV} \quad (3)$$

where I_0 is the saturated CL intensity. Eq. (3) indicates that I_0 is proportional to the initiation rate of ROO• generation induced by UV irradiation. Thus, the evaluation of the durability of PE film against UV is possible using I_0, though it is actually hard to measure exclusively a very weak CL during UV irradiation.

Now, we consider the CL time course after stopping UV irradiation. Since the experimentals were carried out at 25°C, the generation of ROO• by heat could be neglected. Fluorescence and phosphorescence from impurities and PE induced by UV light might be annihilated within several 10 seconds. Then, the observed luminescence is considered to be due to the oxidation reaction induced by UV irradiation. Under this condition, Eq. (2) is rewritten as Eq. (4), and Eqs (1) and (4) give Eq. (5).

$$d[ROO\bullet]/dt = - k_b \cdot [ROO\bullet]^2 \quad (4)$$

$$1/\sqrt{I_{CL}} = \sqrt{k_b/f} \cdot t + 1/\sqrt{I_0} \quad (5)$$

Eq. (5) shows that the reciprocal of the square root of CL intensity after a stop of UV irradiation is proportional to time(t) and the intercept at t=0 gives $1/\sqrt{I_0}$ in the plot of $1/\sqrt{I_{CL}}$ vs t (see Fig. 1). The I_0 value can be determined by this procedure. Fig. 2 shows typical CL decay curves for PE sample as a function of UV irradiation period. The relative CL intensity increased with irradiation period. The plots of $1/\sqrt{I_{CL}}$ vs time for the CL time-course in Fig. 2 were shown in Fig. 3. The $1/\sqrt{I_{CL}}$ showed a good linear relationship with time at the earlier stage of time-course, indicating the validity of Eq. (5).

The CL intensity at t=0, $I_{CL}(t_0)$, was calculated from the intercept of the plot for each sample. As shown in Fig. 4, the

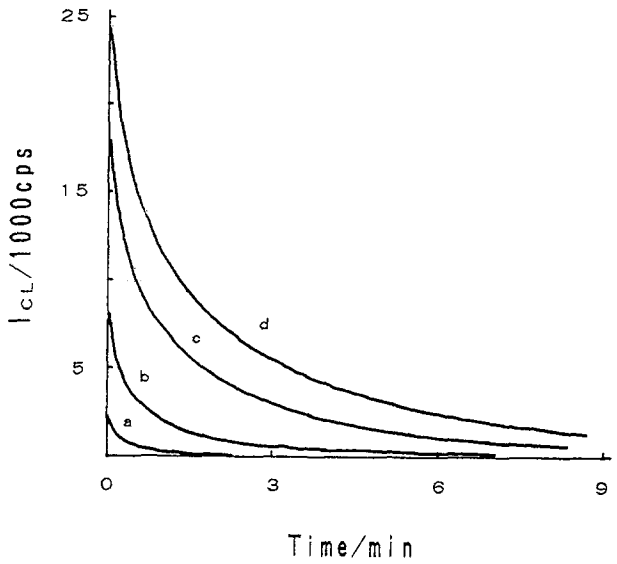

Figure 2 :
Typical UV-induced chemiluminescence time-courses of LLDPE films as a function of UV irradiation period: 15(a), 30(b), 60(c), and 120(d) seconds.

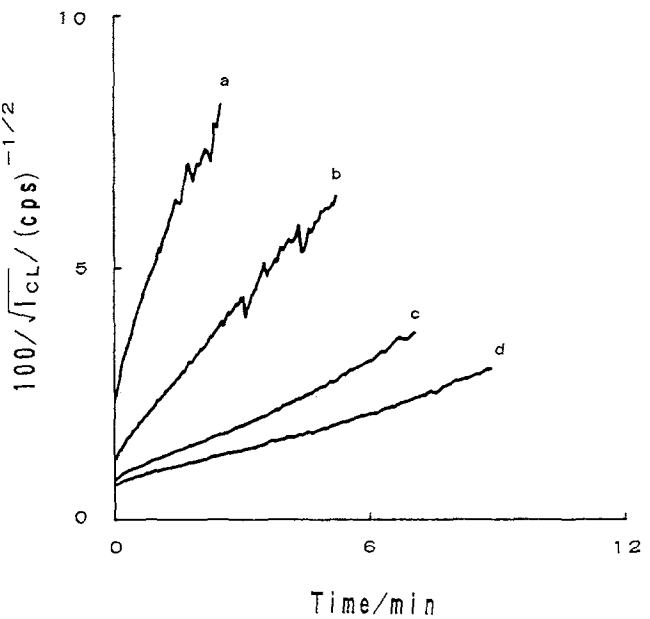

Figure 3 :
Plots of $1/\sqrt{I_{CL}}$ vs time corresponding to Fig. 2, including dead time(30 sec) for CL measurement

$I_{CL}(t_0)$ increased with the irradiation period and gradually saturated at over 60 seconds, which suggests that UV irradiation achieved a steady state for the oxidation induced by UV light. Thus, in this work the satulated CL intensity I_0 was estimated from the CL decay curve after irradiation for 60 seconds.

Table 1
Polyethylene samples and CL parameter I_0 for blown films

sample	MFR[1] g/10min	density[2] g/cm^3	I_0 10^4cps
HP-LDPE-1	2.0	0.924	
without LS[3]			2.65
with LS[3]			1.72
HP-LDPE-2	2.0	0.922	
without LS[3]			0.28
with LS[3]			0.20
L-LDPE-1	0.8	0.921	
without LS[3]			0.70
with LS[3]			0.54

1) measured at 190°C (JIS K6760)
2) measured at 23°C (JIS K6760)
3) Sanol LS944; 1000ppm

Table 1 shows the I_0 for PE films with and without a light stabilizer. PE film with the stabilizer showed smaller I_0 compared to the sample without one. This suggests that the light stabilizer effectively retards the oxidative degradation caused by UV irradiation. The differences in I_0 among three kinds of PE's might be due to the influence of other additives and impurities contained in each sample.
The I_0 for the other kinds of LLDPE films was measured and compared with results of the out-door exposure test. Fig. 5 shows the relation between the I_0 and the durability which is represented as the half-life of tensile elongation. The film having a smaller value of I_0 showed a long life, namely good durability. Judging from the above results, the I_0 is considered to be a valuable parameter to evaluate the durability of PE film against UV irradiation, and it seems advantageous that

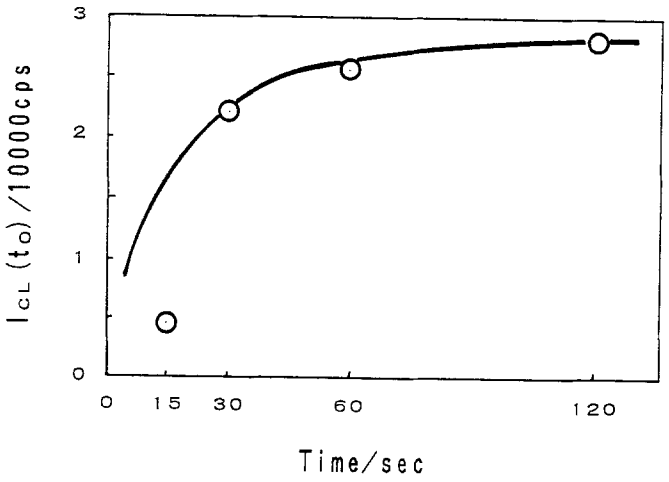

Figure 4 :
UV irradiation time dependence of chemiluminescence intensity of LLDPE film ($I_{CL}(t_0)$) at the start of decay.

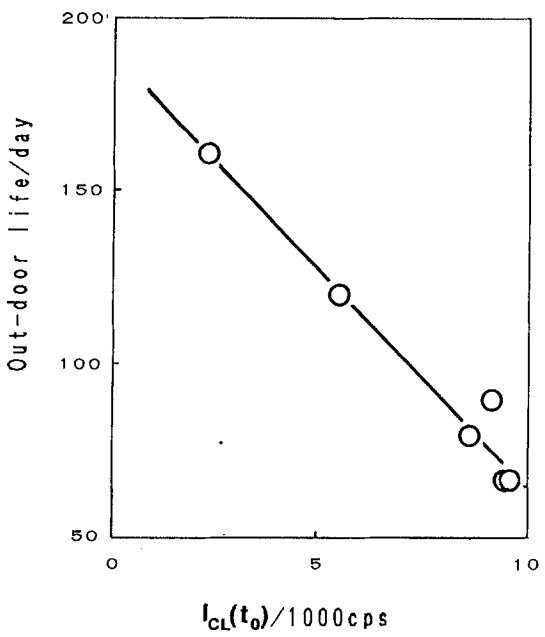

Figure 5 :
Relationship between the CL parameter I_0 and the out-door life for various LLDPE films.

this measurement takes shorter time(~10min) compared to the exposure tests.

Acknowledgments

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