Chapter 8
Thermal Aging of Polyolefin and Effect of Pre-irradiation of γ Ray on Degradation

Masayuki Ito

Abstract The temperature dependence of the thermal aging of ethylene-propylene elastomer (EPR) pure vulcanized and linear low-density polyethylene (LLDPE) was studied using various methods. The activation energy obtained by the measurement of chemiluminescence (CL) of EPR at the constant temperature ranging from 60 to 160 °C was 82.7 kJ/mol. The rate constant of thermal molecular chain scission of EPR was calculated from the chemical relaxation curves measured at constant temperature ranging from 80 to 140 °C. The activation energy was 110 kJ/mol. The total carbonyl concentration increased logarithmically with increased thermal aging from 60 to 160 °C; the activation energy of the rate constant of the carbonyl accumulation was 95.8 kJ/mol. Pre-irradiation on EPR increased the count of CL, the rate of molecular chain scission, and the rate of accumulation of C=O, but the pre-irradiation did not change the values of these activation energies. The weight change of LLDPE resulting from thermal aging was studied at constant temperatures ranging from 90 to 170 °C. Three stages were observed including induction, the weight increase, and the weight decrease period. The activation energy for the induction period was 136 kJ/mol and was 105 kJ/mol for the weight increase. The addition of antioxidant reagent increased the induction period of LLDPE in all of the temperatures, but the activation energy of the induction period was not changed.

When LLDPE was irradiated up to 320 kGy, the induction period of weight change of the sample by thermal aging was remarkably shortened. The mechanism of this result was considered to be as follows. The irradiation of LLDPE in air accumulated hydroperoxide in the samples, which initiated autoxidation of LLDPE rapidly with applying heat.

M. Ito (✉)
Advanced Research Institute for Science and Engineering, Waseda University,
245-26 Nakamachi, Kodaira, Tokyo 187-0042, Japan
e-mail: masayuki@kurenai.waseda.jp

Introduction

Polyolefin is the most widely used polymer in industry and commercial application. Thermal aging is a common in-service degradation mode in the polymer.

The temperature dependence of thermal aging of polyolefin is useful for the short time test and lifetime prediction of the polymer. The recent study pointed out the curvature on the Arrhenius plot of thermal aging of polymer [1]. This article studied the temperature dependence of thermal degradation of ethylene-propylene elastomer (EPR) and linear low-density polyethylene (LLDPE) using various methods. The oxygen uptake in the early period of thermal aging showed the very sensitive method for the evaluation of thermal degradation of polymer [2]. The oxygen uptake in the sample has to increase the weight of the sample; therefore, the weight change along with thermal aging was studied.

Polyolefin is used for an insulating material in the electric cable which is used in nuclear power plants. The electric cable is exposed to radiation and heat simultaneously during the service condition. Dose was estimated to be 500 kGy over 40 years service time [3, 4]. IEEE standards 323-1974 [3] and 323-1978 [4] have provided guides for class IE equipment and electrical type testing. The standards recommend the sequential addition of radiation and heat instead of simultaneous addition, because the sequential method is practically convenient as a test method. In this article, the effect of pre-irradiation of polyolefin on its thermal aging was also studied.

Experimental

Material

Ethylene-propylene elastomer used was commercial grade EP07P and EP11 (JSR, Japan). The molar ratio of ethylene in the copolymer is about 80 % in EP07P and 50 % in EP11. The polymer was mixed with dicumyl peroxide using a mixing roll. The sample was cured by heat press to attain a certain thickness that was different according to the method of measurement. Linear low-density polyethylene (LLDPE) was used for the measurement of weight change along with thermal aging. The different concentration of antioxidant reagent was mixed with LLDPE also using a mixing roll. The antioxidant reagent used was 4,4′-Thio bis (3-methyl-6-tert-butylphenol).

Irradiation

Co-60 γ ray was irradiated to the samples at room temperature in air. Dose rate was 3.0 kGy/h.

Chemiluminescence

Count of chemiluminescence (CL) was measured using a chemiluminescence analyzer OX-7-TC from Tohoku Electric Co. The sample was EP07P having a thickness of about 0.5 mm. The count of CL vs. time was measured at constant temperature ranging from 60 to 160 °C in air. The value of count of CL was extrapolated to time 0, and the value was defined as the initial count of CL.

Rate of Molecular Chain Scission

The rate of molecular chain scission which occurred during thermal aging was obtained by the measurement of chemical stress relaxation [5]. The stress relaxation of EP07P stimulated by heat was measured at different constant temperatures ranging from 80 to 140 °C in air. The thickness of the sample was about 0.5 mm, the width was 5.0 mm, and the distance of jowls was 80 mm. The stress decay was measured at a constant strain (10 %).

Accumulation of Carbonyl Group

The thickness of EP07P used in this experiment was about 0.1 mm. The concentration of generated carbonyl group in the sample by thermal aging was measured using infrared spectrometer type A-32 (JASCO Co.). The concentration of C=O in the film was obtained by using extinction coefficient of 300 L/mol^{-1} cm^{-1} with 1,720 cm^{-1}.

Weight Change

Each sample had a thickness of about 0.15 mm, and a diameter of about 50 mm was placed on the stainless steel pan. Heat aging was performed in an air oven controlled at constant temperature. The weight of the pan with sample was measured periodically by chemical balance at room temperature.

Result

### *Chemiluminescence*

Figure 8.1 shows a relationship between CL count and aging time in the apparatus at 60 °C. Almost the same type of figure was obtained at all of the temperatures from 60 to 160 °C [6]. The count of luminescence is considered to represent the extent of
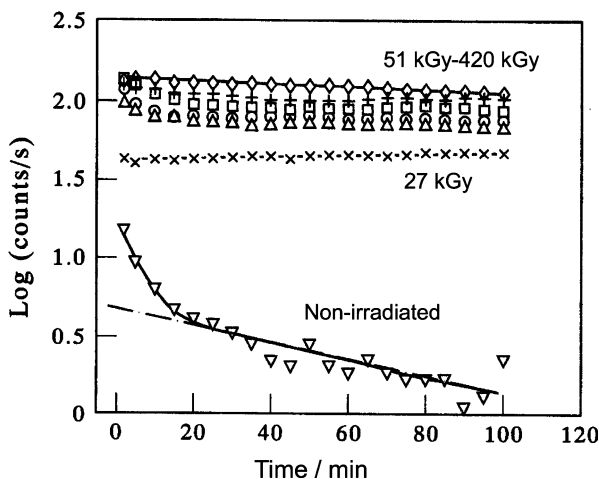
Fig. 8.1 The effect of pre-irradiation on count of chemiluminescence of EP07P at 60 °C

Fig. 8.2 Arrhenius plot of count of chemiluminescence of EP07P
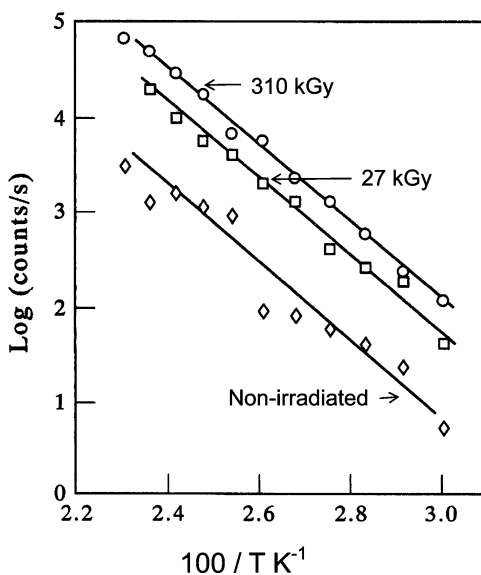
thermal oxidation of polymer [7]. The thermal degradation of polyolefin at 60 °C might be low, but CL sensitively responded to the oxidation as shown in Fig. 8.1.

The CL count increased remarkably by adding samples with a small dose which does not generally affect their mechanical properties. But the amount of emission leveled off at about 50 kGy. This dose consumed the antioxidant reagent added in the production process of EP07P by energy transfer from polymer to antioxidant reagent. The detailed mechanism was reported previously [6].

Figure 8.2 shows the Arrhenius plot of CL count of EP07P. The amount of CL increased by pre-irradiation of γ ray, but the slope was the same as that of the nonirradiated sample; activation energy was 82.7 kJ/mol.
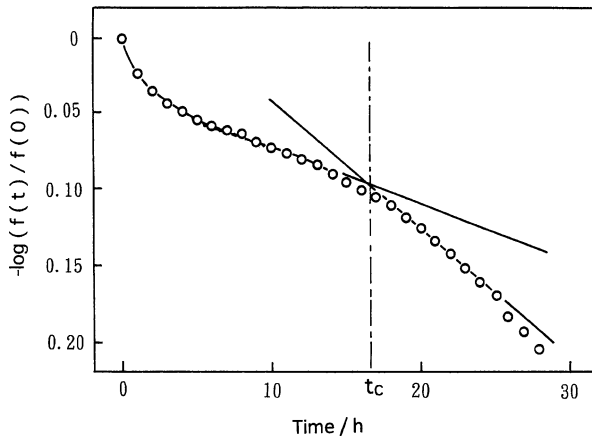
Fig. 8.3 Chemical stress relaxation of nonirradiated EP07P at 100 °C

Rate of Molecular Chain Scission

Figure 8.3 shows the stress-decay curve of EP07P at 100 °C. The rate constant of chemical stress relaxation that is proportional to the molecular chain scission is expressed by Eq. (8.1) [5]:

$$kt = -\log\left(f(t)/f(0)\right) \tag{8.1}$$

where k is the rate constant of chemical stress relaxation, $f(0)$ is the initial stress under the constant strain, and $f(t)$ is the stress at time t. The slope of the curve in Fig. 8.3 is considered to be proportionate to the rate of molecular chain scission. The very early stage of stress decay is due to the physical flow of molecular chain.

The slope of curve in Fig. 8.3 increased at time tc. This phenomena means that the effect of small amount of antioxidant reagent which was added in the production process of EP07P to prevent oxidative degradation during storage of the sample was decreased by thermal aging and the rate of molecular chain scission increased from tc.

The stress relaxation curves obtained at 110, 120, 130, and 140 °C are shown in Fig. 8.4. The value tc was observed in all of the decay curves [8]; the time associated with tc might be comparable to the lifetime of the effect of the antioxidant reagent added in the production process. The Arrhenius plot of tc is shown in Fig. 8.5; activation energy is 116 kJ/mol.

The effect of pre-irradiation on thermal aging of EP07P is shown in Fig. 8.6. This figure shows the stress-decay curves of EP07P which was irradiated up to 50 kGy. The decay curves are straight line; tc was not observed on the curves when sample was pre-irradiated. The chemical stress relaxation curves of the sample which was irradiated up to 96 kGy showed the same decay curves as that irradiated up to 50 Gy [8].
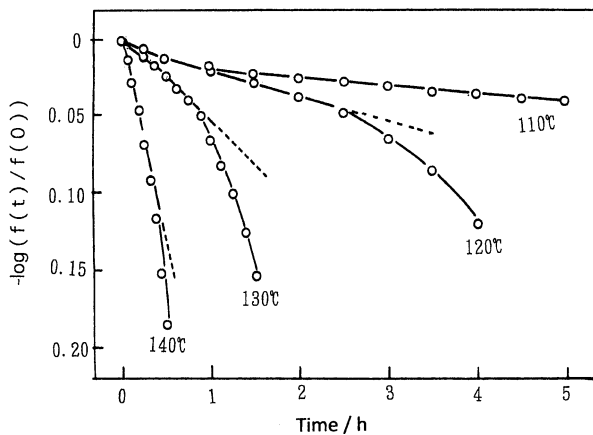
Fig. 8.4 Chemical stress relaxation of nonirradiated EP07P at various temperatures
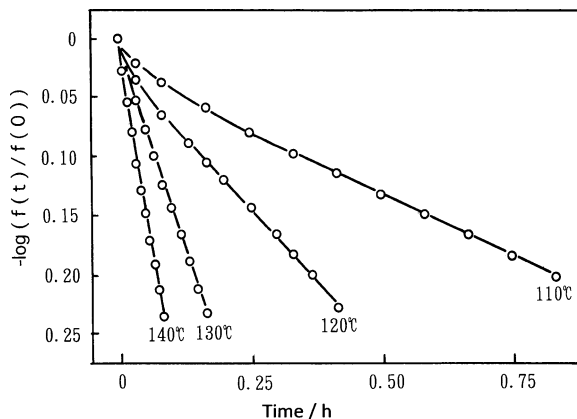

Fig. 8.5 Arrhenius plot of tc of nonirradiated EP07P
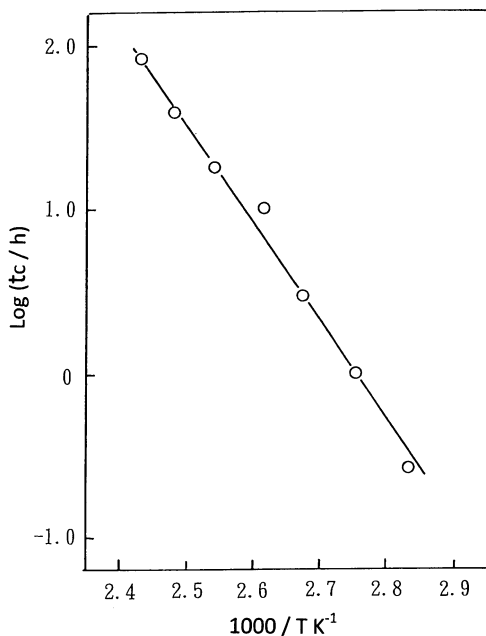
The rate of thermal chain scission Qm(t)/t is expressed by Eq. (8.2) [5]:

$$Qm(t)/t = -N(0)\ln(f(t)/f(0))/t \tag{8.2}$$

where $N(0)$ is the initial network concentration of the elastomer, which was calculated from the initial modulus of the samples [8].

Fig. 8.6 Chemical stress relaxation of pre-irradiated EP07P at various temperatures

Table 8.1 Rate constant of thermal molecular chain scission of EP07P which has various thermal and irradiation histories (mol h^{-1} ml^{-1})

Temperature (°C)	Dose (kGy)			
	0 (before tc)	0 (after tc)	50	96
80	6.1×10^{-7}	6.6×10^{-7}	5.5×10^{-6}	4.3×10^{-6}
90	8.5×10^{-7}	1.5×10^{-6}	1.8×10^{-5}	1.3×10^{-5}
100	2.1×10^{-6}	4.0×10^{-6}	4.8×10^{-5}	3.8×10^{-5}
110	3.4×10^{-6}	9.9×10^{-6}	1.1×10^{-4}	9.2×10^{-5}
120	9.4×10^{-6}	2.2×10^{-5}	2.4×10^{-4}	2.3×10^{-4}
130	3.6×10^{-5}	7.4×10^{-5}	7.0×10^{-4}	5.3×10^{-4}
140	1.4×10^{-4}	2.2×10^{-4}	1.4×10^{-3}	1.4×10^{-3}

Table 8.1 shows the rate constant of thermal chain scission of EP07P before tc, after tc, and pre-irradiated up to 50 and 96 kGy. The rate of thermal chain scission after tc was about twice that before tc. Irradiation decupled the rate constant of the decay, but the rate constant did not increase even though the dose increased from 50 to 96 kGy.

Figure 8.7 shows the Arrhenius plot of the rate of thermal chain scission of EP07P which was measured before and after tc. The obtained line had the same slope, and activation energy was 110 kJ/mol.

The effect of pre-irradiation on activation energy is not observed as shown in Fig. 8.7.

Accumulation of Carbonyl Group

Oxidation of hydrocarbon produces carbonyl and carboxyl group in the material. These functional groups affect the electric properties of the sample. Therefore, the concentration of C=O produced along with aging may be an indicator of the degree of degradation of polyolefin.

Fig. 8.7 Arrhenius plot of
rate of chain scission of
EP07P
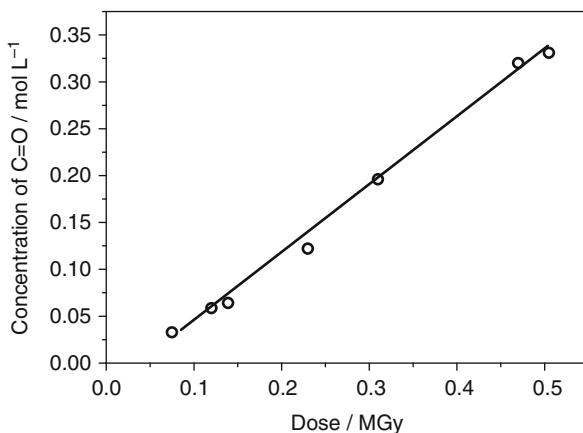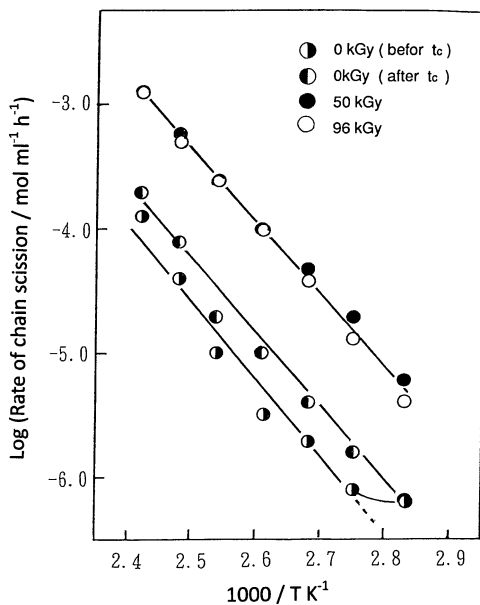
Fig. 8.8 Relationship between dose and C=O accumulated in EP07P by irradiation of γ ray

Figure 8.8 shows the relationship between dose and concentration of C=O. The concentration of C=O linearly increased with increasing dose. The samples that have different irradiation dose were thermally aged at 110 °C, and the result is shown in Fig. 8.9. The concentration of C=O exponentially increased with increasing thermal aging time. The point of curvature was observed when the samples which had low pre-irradiation dose were thermally aged. When pre-irradiation dose was more than 60 kGy, there was no curvature on the line. This suggests the following process.
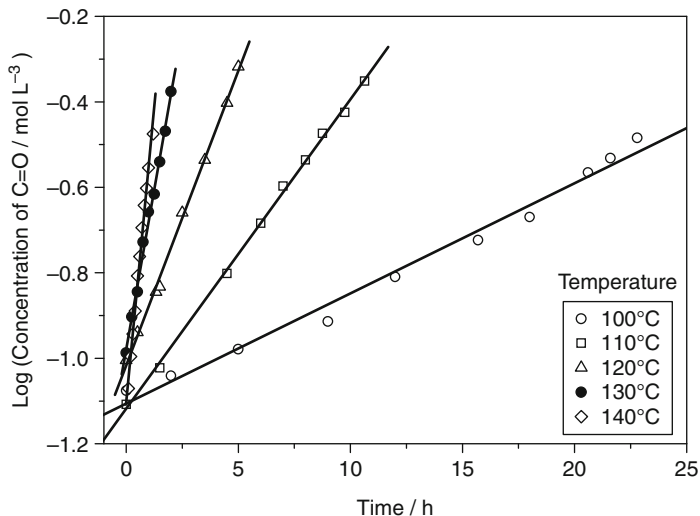
Fig. 8.9 Effect of dose on the increase in the concentration of C=O in EP07P by thermal aging at 110 °C
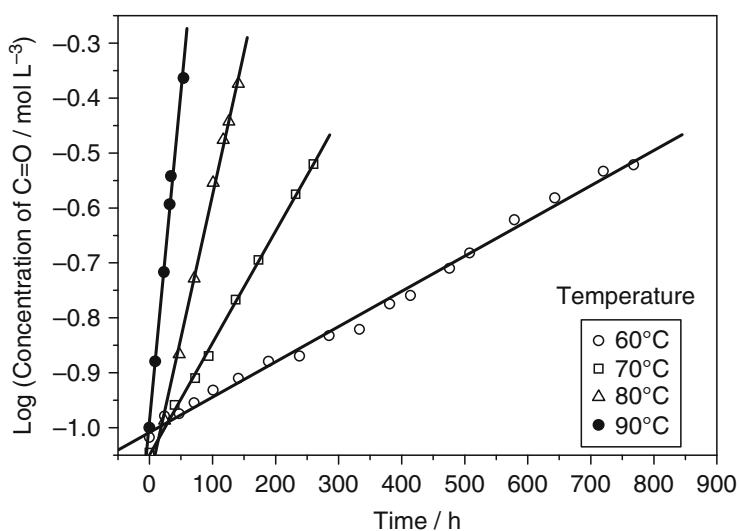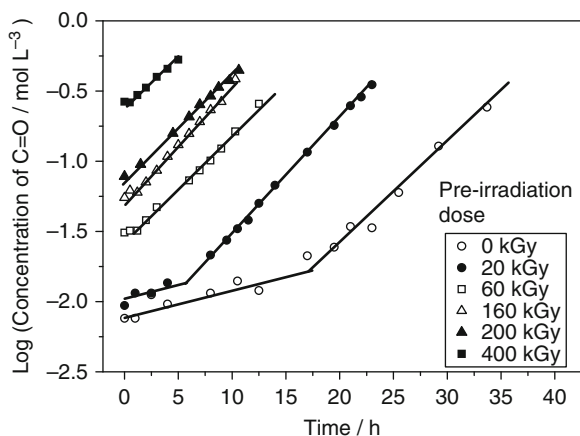
Fig. 8.10 Increase in the concentration of C=O in EP07P irradiated up to 200 kGy by thermal aging at relatively low temperatures

A small amount of antioxidant reagent added in the production process of EP07P depresses the thermal oxidation of the polymer. However, 20 h of thermal aging at 110 °C or irradiation at about 60 kGy consumed the antioxidant reagent in the sample. The rate of autoxidation at the constant temperature depends on whether the antioxidant reagent exists or not.

Figures 8.10 and 8.11 show an increase in C=O along with thermal aging at 60, 70, 80, 90, 100, 110, 120, 130, and 140 °C, respectively. All of the samples were irradiated up to 200 kGy; there might be no antioxidant reagent in those samples.

Fig. 8.11 Increase in the concentration of C=O in EP07P irradiated up to 200 kGy by thermal aging at relatively high temperatures

Fig. 8.12 Arrhenius plot of K
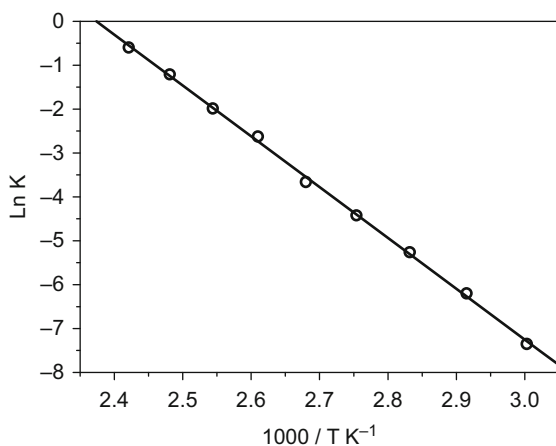
The rate constant of total carbonyl accumulation in the sample is expressed by Eq. (8.3):

$$\text{Log}C = Kt \qquad (8.3)$$

In Eq. (8.3), C is the concentration of C=O observed by IR spectrometer, t is the thermal aging time, and K is the rate constant of total carbonyl accumulation in the sample.

Figure 8.12 shows the Arrhenius plot of K; the straight line was obtained from 60 to 140 °C; the activation energy is 95.8 kJ/mol.
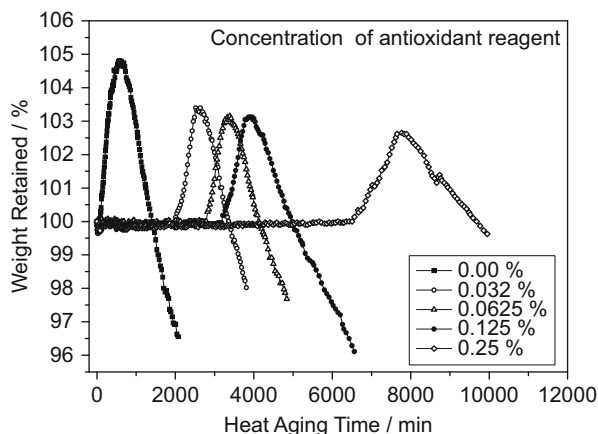
Fig. 8.13 The effect of the concentration of antioxidant reagent on weight change of LLDPE at 150 °C
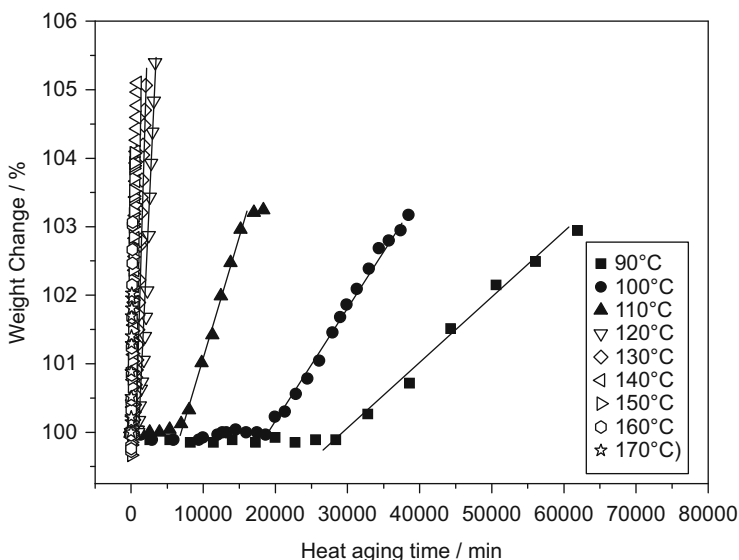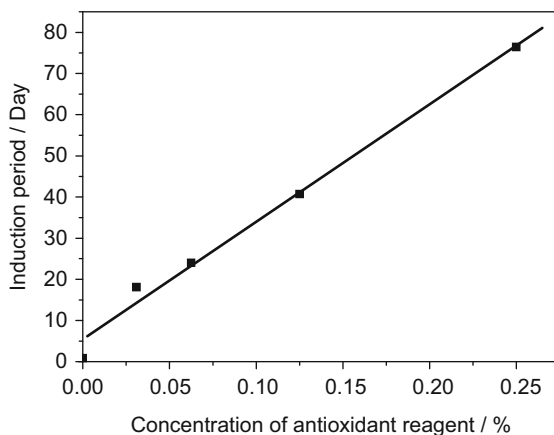
Weight Change

Thermogravimetry (TG) has been widely used for evaluating the heat-resistant properties of polymers [9–15]. In this method, the weight of samples was continuously measured as the temperature of the sample was raised at a constant rate. TG method is based on the analysis of the weight decrease curve accompanying the thermal decomposition of samples during heat aging. But when thermal aging takes place in air, oxidative products accumulate in the polymer. This increases the weight of the polymer.

For a quantitative analysis of the oxidative reaction of polymer, the accurate measurement of the weight change at a constant temperature might be more useful than TG method. The previous article [16] studied the induction period, the increase in weight, and the weight decrease of EP07P along with isothermal aging; the activation energy of each stage of the thermal aging, induction period, weight increase, and weight decrease, was also investigated.

This article studied the weight change of LLDPE by thermal aging at constant temperatures. The effect of the concentration of antioxidant reagent on the weight change by thermal aging was also investigated. Figure 8.13 shows the weight change of LLDPE by thermal aging at 150 °C. The induction period where the weight of sample was kept constant in early period of thermal aging depends on the concentration of antioxidant reagent. On the other hand, the significant difference on the effect of the concentration of antioxidant reagent was not observed on the slope of weight increase curve.

The same result was obtained on the relationship between weight change and aging time at various temperatures ranging from 90 to 170 °C. The detail will be reported in the future. The effect of the concentration of antioxidant reagent on the

Fig. 8.14 Relationship
between the concentration of
antioxidant reagent and the
induction period on the
thermal aging of LLDPE at
120 °C

Fig. 8.14 chart: X-axis "Concentration of antioxidant reagent / %" from 0.00 to 0.25; Y-axis "Induction period / Day" from 0 to 80.

Fig. 8.15 chart: X-axis "Heat aging time / min" from 0 to 80000; Y-axis "Weight Change / %" from 100 to 106. Legend: ■ 90°C, ● 100°C, ▲ 110°C, ▽ 120°C, ◇ 130°C, ◁ 140°C, ▷ 150°C, ○ 160°C, ☆ 170°C).

Fig. 8.15 Initial sage of weight change of EP07P in which antioxidant reagent was not added at various temperatures

induction period at 120 °C is shown in Fig. 8.14 as one of the examples; the induction period was proportional to the concentration of the antioxidant reagent.

Figure 8.15 shows the initial stage of weight change of LLDPE by thermal aging at various temperatures ranging from 90 to 170 °C. The Arrhenius plot of the induction period of the samples which have different concentration of antioxidant reagent was shown in Fig. 8.16. The slope of the lines was almost the same. The apparent activation energy was 136 kJ/mol.

Figure 8.17 shows the Arrhenius plot of the rate of weight increase of the sample by thermal aging. The activation energy was 105 kJ/mol, which does not appear to depend on the concentration of antioxidant reagent.

Fig. 8.16 Arrhenius plot of thermal aging of LLDPE which contains various antioxidant concentrations
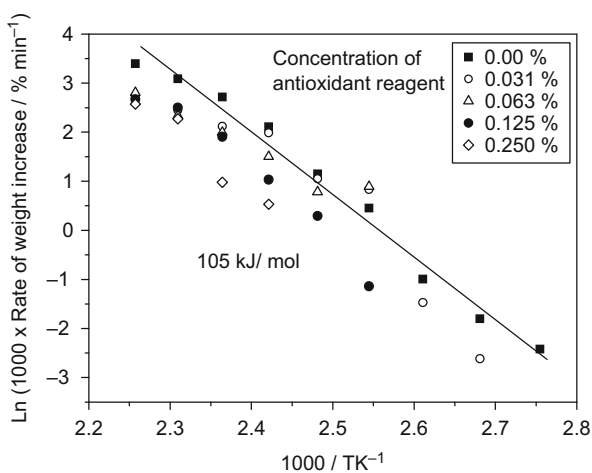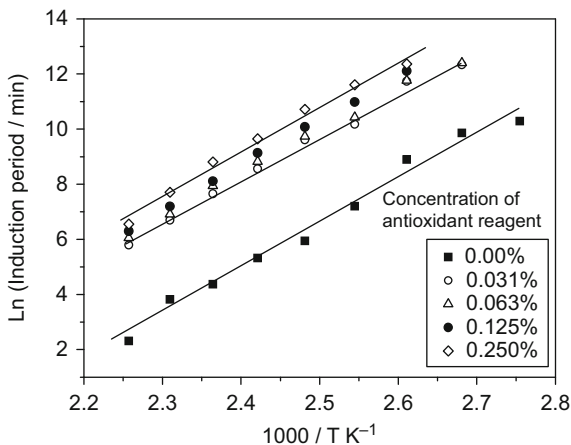
Fig. 8.17 Arrhenius plot of the weight increase of LLDPE which contains various antioxidant concentrations

Effect of Pre-irradiation of γ Ray on the Thermal Aging of LLDPE

When the polyolefin was exposed to heat after irradiation, the heat-resistant properties are affected by the irradiation. Figure 8.18 shows the effect of pre-irradiation on weight change of LLDPE by thermal aging at 150 °C. Dose of pre-irradiation was 320 kGy.

The pre-irradiation resulted in the remarkable changes on the behavior of thermal aging of LLDPE even though the thermal aging condition shown in Fig. 8.18 is the same as that shown in Fig. 8.13. The induction period of weight increase was very
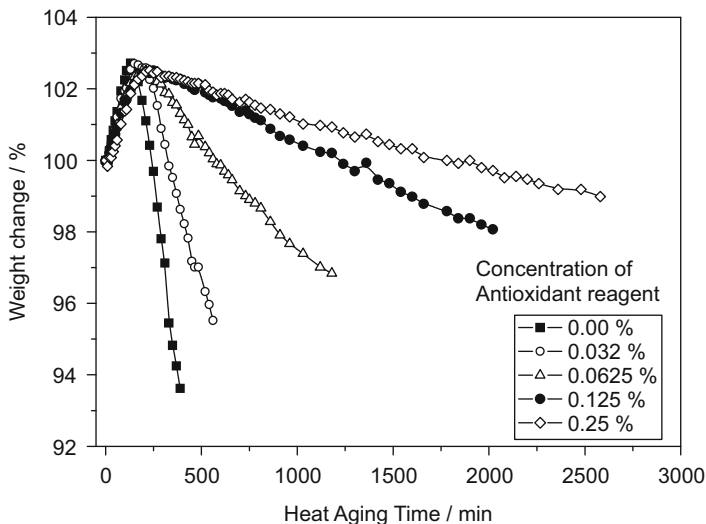
Fig. 8.18 The effect of pre-irradiation on weight change of LLDPE. The dose was 320 kGy

short, and the effect of concentration of antioxidant reagent was not observed in the induction period. The rate of weight decrease depended on the concentration of antioxidant reagent. This phenomenon was different from the result obtained for the nonirradiated samples shown in Fig. 8.13.

Discussion

Activation Energy of Thermal Aging of EP07P Obtained by Various Methods

Phenomenology as proposed by Edmund Husserl (1859–1938) can be roughly described as the sustained attempt to describe experiences without metaphysical and theoretical speculations. His idea on the relationship between an appearance and the phenomenon could be considered that the measurement by a certain method gives only an appearance of the phenomenon.

When we study the temperature dependence of the thermal aging of polymer, the obtained activation energy is considered to be an appearance of the phenomenon, i.e., the thermal aging in this study. To understand the phenomenon which occurred during thermal aging, it is useful to compare the values of activation energy obtained by various methods for one polymer.

Table 8.2 shows activation energy of thermal aging of EP07P. The value was different to the different method of measurement. The count of CL represents the

Table 8.2 Activation energy of thermal aging of EP07P obtained by various methods

Focused point	Activation energy (kJ/mol)
Induction period[a]	113
Rate of weight increase[a]	113
Slope of weight loss[a]	60.3
Chemiluminescence (oxidation)[b]	82.7
Rate of thermal chain scission[c]	110
Accumulation of C=O	95.8

[a]M. Ito, S. Inayoshi and K. Moriyama, Polymer degrad. and Stab., 93, 1935 (2008)
[b]M. Ito: Radiat. Phys. Chem. 41, 443 (1993)
[c]M. Ito, T. Sato and K. Murakami: Soc. Japan Rubber Indust. 69, 98 (1996)

Table 8.3 Activation energy of thermal aging of polyolefin obtained by the measurement of weight change

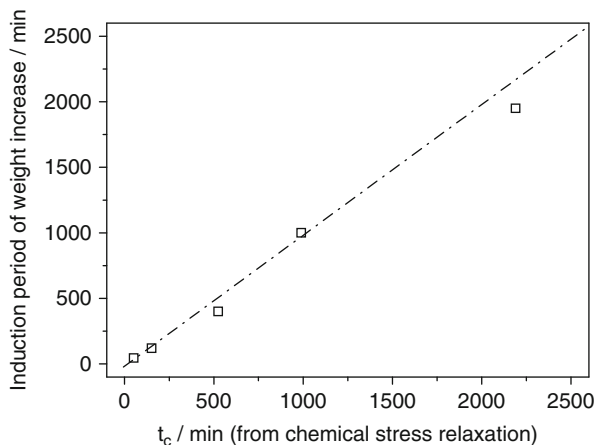| Sample	Induction period	Wight increase	Wight decrease
LLDPE	136 kJ/mol	105 kJ/mol	153 kJ/mol
EP11	110 kJ/mol	50 kJ/mol	
EP07P[a]	113 kJ/ mol	113 kJ/mol	60.3 kJ/mol

[a]Masayuki Ito, Shigekazu Inayoshi and Kentaro Moriyama Polymer degrad. and Stab., 93 (2008) 1935-1938

amount of oxidation occurred at the temperature but the count of CL dose not reflects changes in molecular structure of polymer. The increase in total carbonyl affects the electric properties of the sample, and therefore, this activation energy might be applicable in the field of electric engineering. The scission of molecular chain deteriorates the mechanical properties of polymer. The activation energy obtained by the measurement of chemical stress relaxation might be applicable to deciding the condition of short time test by heat when the mechanical properties were focused on. As seen above, it is useful to pile up the value of activation energy obtained by the measurement of various appearances.

Activation Energy of Thermal Aging of Polyolefin

Table 8.3 shows the activation energy obtained by the measurement of weight change of two kinds of EPR and LLDPE. The values in the weight increase and the weight decrease were largely different to the different sample but the induction period showed relatively near value each other.

The most likely reason might be as follows. The basic mechanisms consist of an initiation step in which hydrogen is removed from molecule leaving the free radical. This radical react with oxygen to form a peroxy radical and the autoxidation is started. The temperature dependence of these reactions is the same in the simple polyolefin.

Fig. 8.19 The relationship between curvature tc from where the rate of chain scission increased and the induction period of weight increase of EP07P

The Relationship Between tc and the Induction Period

Figure 8.19 shows the relationship between the induction period of weight change of EP07P and the time tc which was obtained from chemical stress relaxation curve of the elastomer. The temperature range was between 90 to 130 °C. Both values had the same period of time as shown in this figure.

This reason is considered as follows. The small amount of antioxidant reagent was consumed by thermal aging at this period and thermal oxidation increased. This brought about the increase in the rate of chain scission and addition of carbonyl groups.

Analytical View on the Weight Change of Polyolefin by Thermal Aging

Three stages were observed on the weight change of polyolefin, i.e., the induction period, the period of weight increase, and the period of weight decrease. The mechanism of weight change of EP07P might be explained as follows.

In the initial stage, molecular chain scission was started, but the rate of scission was low before tc. The accumulation of carbonyl went on in this stage, but the concentration of C=O increased logarithmically with increasing aging time. Therefore, the reactions which occurred in the initial stage didn't have an effect on the weight of the sample.

In the second stage, the accumulation of C=O increased the weight of the sample. The scission reaction increased after tc, but the molecular chain fragment which was generated by thermal aging kept the relatively longer chain length and was not evaporated from the sample at the temperature. As a result, the weight of sample increased with increasing aging time in this stage.

In the third stage, the scission reaction generated shorter molecular chain in the sample, some of which contain C=O group in the molecule. Finally, this stage severely reduced the length of molecular chain which evaporated from sample to air at the temperature.

Effect of Pre-irradiation of Polyolefin on Thermal Aging

The relationship between weight change of LLDPE and thermal aging time is shown in Figs. 8.13 and 8.18 for the sample of nonirradiated and pre-irradiated, respectively. The irradiation shortened the induction period of the samples which contain various concentrations of antioxidant reagent. As shown in Fig. 8.18, the induction periods of all of the samples are the same.

It is solved that the difference between the result of nonirradiated samples and pre-irradiated sample might be as follows.

In the very early stage of thermal aging of PE, the radical concentration was very low. It takes a certain period of time to accumulate even low concentration of peroxide in the nonirradiated PE, which initiates autoxidation. Irradiation even at room temperature generates higher concentrations of radicals in the samples. The radicals react with oxygen in air, and hydroperoxide is produced and accumulated in PE. This hydroperoxide initiates autoxidation at the initial stage of thermal aging. The weight increase by the accumulation of carbonyl was stated from very early period of thermal aging as shown in Figs. 8.9 and 8.18.

Index of Lifetime Prediction

The activation energy is the important factor in estimating the lifetime of polyolefin along with thermal aging. The value was obtained by the measurement of rate of the weight increase and weight decrease, the rate of molecular chain scission, the accumulation of total carbonyl, and counts of CL. The point of curvature of measured value on the time scale of thermal aging is essential for predicting the lifetime of polymer.

The induction period is obtained by a simple method, i.e., the measurement of the weight of sample along with thermal aging might be one of the useful indicators for the lifetime prediction. In the future, it is expected to investigate the relationship between the induction period and the changes in practical performance of the polymer on the course of thermal aging.

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