

Review

Degradation of Dielectric Properties of Polyethylene by Combination of γ -Irradiation and Thermal Aging

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It has been found that the application order of thermal aging and γ -irradiation causes a different degradation of mechanical properties of insulating materials. In this review, we focus in depth on oxidative degradation and degradation of dielectric properties of polyethylene under combined thermal aging and γ -irradiation. To exclude the effect of additive agents and to minimize the effect of the process limited by diffusion of oxygen on degradation, a 25 μm thick low-density polyethylene film free from additives has been used.

It has been clarified that the simultaneous application of thermal aging and γ -irradiation causes the most oxidative degradation, while the single application of γ -irradiation exhibits the largest loss tangent on dielectric property for the same oxidative degradation. According to the order of the application of thermal aging and γ -irradiation, there is a great differences of oxidative degradation and degradation of dielectric properties. The results have been also explained in terms of gel fraction and crosslinking.

Key Words: polyethylene, nuclear power generating station, cable, degradation, dielectric property, oxidation

1. Introduction

Electrical cables used in nuclear power generating stations are required to maintain their functions even if the nuclear reactor encounters a loss of coolant accident at the end of installed life. The basic requirements for these cables are described in the IEEE Standards 323(1974) and 383(1974).^{1,2)} At the present time, the above testing methods have been used in Japan. The IEEEJ set up a technical committee for studying cables and wires in nuclear

generating stations and it has presented the recommended method of cables for safety systems in nuclear power generating stations.³⁾ These standards will be revised to be more strict with the development of further studies.

Generally, degradation of mechanical properties for organic insulating materials under the combined environment of γ -irradiation and thermal aging has been used as a measure of degradation. Degradation study of mechanical properties of organic insulating materials under the combined environment of γ -irradiation and thermal aging can yield valuable data. It should be noted that the other properties of electrical insulating materials may be of equal engineering significance and should be studied.

The order of application of thermal aging and γ irradiation on the degradation of mechanical properties has been found significant.^{4,5)} It has been found that volatilization or consumption of anti-oxidant or anti-radiation agent causes a different degradation of mechanical properties according to the order of application of the treatments. On the other hand, the evaluated subjects or criteria for the thermal aging degradation during normal operation for the above methods have not been mentioned clearly in the standards. It is well known that the electrical properties of insulating polymers are related to various of mechanical properties. At the present time, the change of elongation is often used as a criterion for the degradation. Elongation rate of polyethylene (PE), crosslinked PE (XLPE), and anti-flamed XLPE is decreased with irradiation dose. Although irradiation in vacuo causes crosslinking and scission of molecular chain, the chain scissions happen after oxidative degradation in air. A ratio of chain scission to crosslinking increases with irradiation dose; therefore, the elongation rate decreases with irradiation dose. Mechanical properties have been investigated under irradiation exposure on a sheet 1 mm thick and depend on radiation rate because of the process limited by oxygen diffusion.⁶⁾

To exclude the effect of additive agents and to minimize the effect of the process limited by diffusion of oxygen on the degradation, a 25 μ m thick low density PE film free from additives has been used. We have already discussed degradation of PE films by combination of thermal aging (90 °C & 7 days) and γ -irradiation exposure (10 Mrad).⁷⁾ The results have been discussed from the points of view of dielectric loss tangent and infrared absorption and we show that the degradation is affected by the order of application of thermal aging and irradiation exposure.

In the present review, we focus in depth on oxidative degradation and degradation of dielectric properties of polyethylene under the combined environment of γ -irradiation and thermal aging.^{8,9)} Oxidative degradation and degradation of dielectric properties of polyethylene have been discussed under the expanded conditions of thermal aging and irradiation dose.

2. Samples and Experiments

Low-density polyethylene (abbreviated LDPE; ZF-30, Mitsubishi Petrochemical Co., Ltd.) films free from additives were used, having density

of 0.92 g/cm^3 , melting point of 110°C and crystallinity of about 50 %. In this experiment, an aging temperature of 90°C was chosen as the highest possible, since the melting point of LDPE is 110°C . Thermal aging (denoted as HT) was made in air. The thermal aging time t_{HT} was chosen as 7 days. Irradiation exposure with γ -rays from Co^{60} source (denoted as γ) was carried out at a dose rate of $5.02 \times 10^4 - 5.3 \times 10^4 \text{ rad/h}$ at room temperature in the presence of air, varying the radiation period, t_r . Five kinds of samples were prepared by the single-, sequential- or simultaneous-exposure of γ and HT, such as (HT), (γ), (HT- γ), (γ -HT) and ((γ , HT)) samples, where the bar (-) means the order of the application, and ((γ , HT)) means the simultaneous application of γ and HT. The value of t_{HT} for the ((γ , HT)) sample is approximately estimated as (irradiation dose)/(dose rate). Table 1 shows the description for the prepared samples and the symbols used in the following Figures (except Fig. 14). Otherwise, thermal aging time t_{HT} (h) for HT and irradiation exposure period t_r (h) are properly presented.

Table 1 Symbols for variously treated samples and in Figures.

symbols	conditions	symbols in Figs.
(HT)	thermal aging for t_{HT} (hr) at 90°C in air	□
(γ)	γ -irradiation for t_r (hr) at room temperature in air	○
(HT- γ)	γ -irradiation after thermal aging ($t_{HT} = 168 \text{ hr}$)	△
(γ -HT)	thermal aging for t_{HT} (hr) after γ -irradiation	$t_{HT} = 168 \text{ hr}$ ▲ $t_{HT} = t_r$ ▼ otherwise △
((γ , HT))	simultaneous application of thermal aging and γ -irradiation (γ -irradiation was made at 90°C , $t_{HT} = t_r$)	●

Infrared absorption for the samples as shown in Table 1 was measured with an infrared spectrometer (A-100, Japan Spectroscopic Co., Ltd.). The absorption coefficient α of carbonyl groups was estimated at 1715 cm^{-1} from the base line method on the infrared spectrum.

Dielectric properties were measured using a transformer bridge (1621 Precision Capacitance System; General Radio Co., Ltd.). The dielectric measurements were performed over the temperature range from -90°C to $+90^\circ\text{C}$.

The gel fraction was measured with a Soxhlet extractor using toluene as a solvent. After the virgin sample with a weight from 0.48 to 0.50 g had been extracted for 10 h, the gel fraction was estimated from the dried insoluble residuum.

3. Experimental Results

3.1 Oxidative Degradation

Figure 1 shows an absorption coefficient α of carbonyl groups for (γ),

(HT- γ), (γ -HT), and ((γ , HT)) samples as a function of irradiation dose. In each case the value of t_{HT} is 168 h, except for the ((γ , HT)) sample, where t_{HT} can be estimated from the ratio of (irradiation dose)/(dose rate). Although the irradiation was sometimes interrupted by circumstances of running, the relation $t_{HT} = t_r$ is held approximately constant.

The values of α for the (γ) sample show an increase with incremental irradiation dose. Features of the other samples are as follows: The value of α of the (HT- γ) sample is larger than that for the (γ) one when the irradiation dose is less than 10 Mrad, but they are almost same each other when irradiation dose is beyond 10 Mrad. The value of α for the (γ -HT) sample is larger than those of the (γ) and the (HT- γ) samples. The values of α for the ((γ , HT)) sample are larger than that of the (γ) and the (HT- γ) samples, but the comparison between the (γ -HT) and the ((γ , HT)) samples indicates that the value of α for the latter is larger than that for the former beyond an irradiation dose of 10 Mrad.

Figure 2 shows the values of α for the (γ -HT) sample under the condition of $t_{HT} = t_r$ as a function of irradiation dose. Also for reference, the results of the ((γ , HT)) sample, which approximately holds the relation of $t_{HT} = t_r$, are presented in Fig. 2. In the case of $t_{HT} = t_r$, there is no remarkable difference for the value of α between the (γ -HT) and the ((γ , HT)) samples.

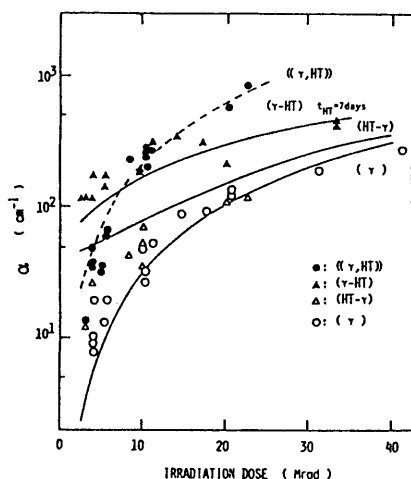


Fig. 1 Absorption coefficient α of carbonyl groups as a function of irradiation dose. ($t_{HT} = 168$ h).

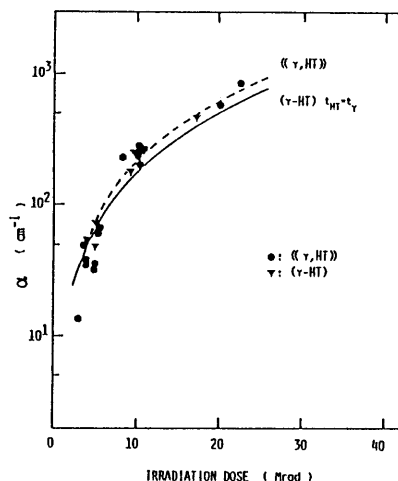


Fig. 2 Absorption coefficient α of carbonyl groups for ((γ , HT)) and (γ -HT) samples as a function of irradiation under the condition of $t_{HT} = t_r$.

Figure 3 shows the variation of α for the (γ -HT) sample as a function of t_{HT} . Also, the value of α at $t_{HT} = 0$ for the (γ -HT) sample corresponds to that for the (γ) sample. The value of α for the (γ -HT) sample rapidly increases. An offset $\Delta\alpha(t_{HT}) = \alpha(t_{HT}) - \alpha_0(t_{HT} = 0)$, due to by thermal aging, is shown as a function of Δt_{HT} in Fig. 4, where Δt_{HT} has the same meaning as t_{HT} . In Fig. 4, the function $\Delta\alpha = \alpha(t_{HT}) - \alpha(t_{HT=0})$ for the (HT) sample, where $\alpha(t_{HT=0})$ has the same value as α with the (γ) sample of irradiation dose of 9.2 Mrad, is shown by the dotted line as a function of $\Delta t_{HT} = t_{HT} - t_{HT=0}$. It is clear that even when the (γ) and the (HT) samples have the same value of α , the value for the former rapidly increases upon thermal heating as compared with that for the latter.

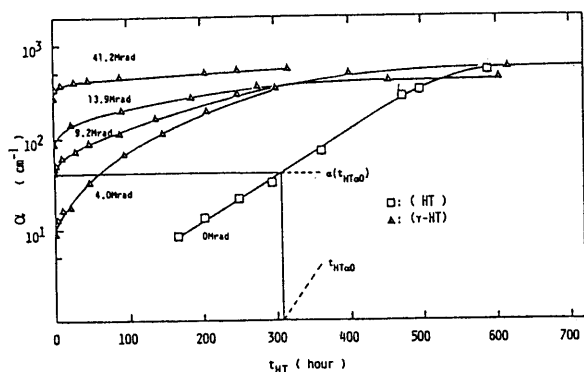


Fig. 3 Absorption coefficient of carbonyl groups for (HT) and (γ -HT) samples as a function of t_{HT} .

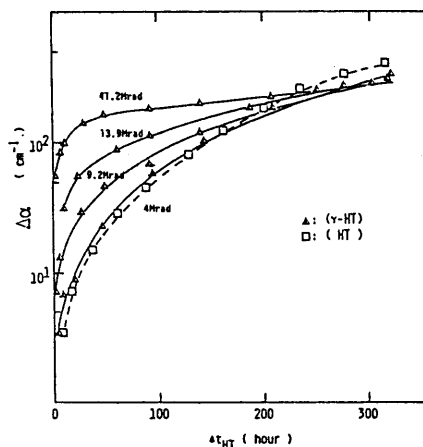


Fig. 4 Increment of $\Delta\alpha$ of absorption coefficient of carbonyl groups by thermal aging for (γ) samples as a function of Δt_{HT} .

3.2 Dielectric Properties

Figures 5(a) and (b) show typical dielectric properties of relative permittivity, ϵ_r' , and dielectric loss factor, ϵ_r'' , of the (γ) sample irradiated with 20 Mrad. The value of α is 119 cm^{-1} . It is seen that the maximum dielectric loss factor for the 1 kHz curve appears around 10°C . Usually, the glass transition of LDPE occurs near -23°C at 1 kHz. Although the relaxation peak in the ϵ_r' vs. T characteristics seems to be due to the primary dispersion, which can be related to the glass transition, the peak temperature of 10°C is much higher than the ordinary glass transition temperature of LDPE. The values of ϵ_r' and dielectric dissipation factor ($\tan \delta$) for the (γ) sample at room temperature are estimated from the 1 kHz curve in Figs. 5 as 2.55 and 6.3×10^{-3} , respectively. These values are larger than that of 2.25 to 2.35 and a well-known value of $\tan \delta$, less than 5×10^{-4} .

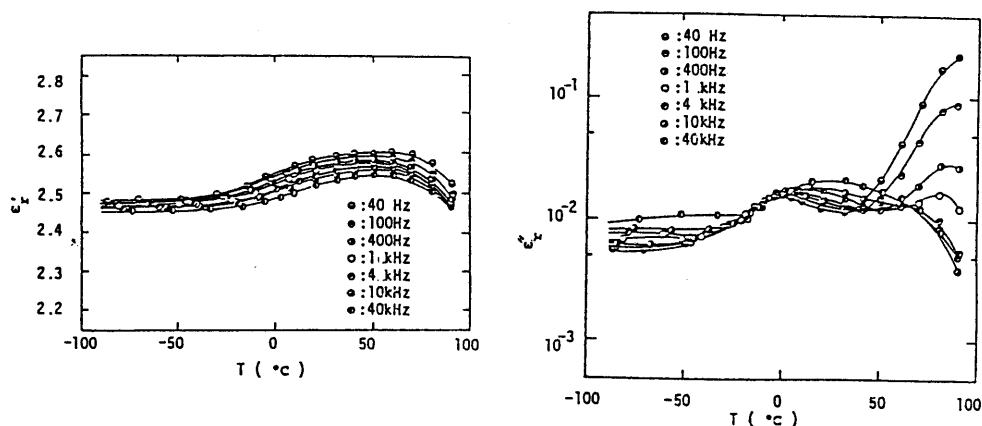


Fig. 5 Typical dielectric properties ϵ_r' (a) and ϵ_r'' (b) of (γ) sample. (irradiation dose is 20 Mrad)

for an as-received LDPE, respectively.

The maximum values of $\tan \delta$, $\tan \delta_{max}$, at 1 kHz, as read from $\tan \delta$ vs. T curves are shown in Fig. 6 as a function of irradiation dose. It can be seen that $\tan \delta_{max}$ for the (γ) sample increases with increasing irradiation dose. The values of $\tan \delta_{max}$ for the (γ) sample are almost equal to those for the (HT- γ) sample. The values of $\tan \delta_{max}$ for the (γ -HT) sample also increases with irradiation dose and are larger than those for the (γ) and (HT- γ) samples. The ((γ , HT)) sample has a smaller value of $\tan \delta_{max}$ than the (γ -HT) sample when the irradiation dose is less than 4 Mrad, but the former sample shows the largest value of $\tan \delta_{max}$ among the samples beyond an irradiation dose of 4 Mrad. Because t_{HT} for the ((γ , HT)) sample increases with irradiation dose, a change in t_{HT} with irradiation especially above 4 Mrad may influence the value of $\tan \delta_{max}$. The results of $\tan \delta_{max}$ in Fig. 6

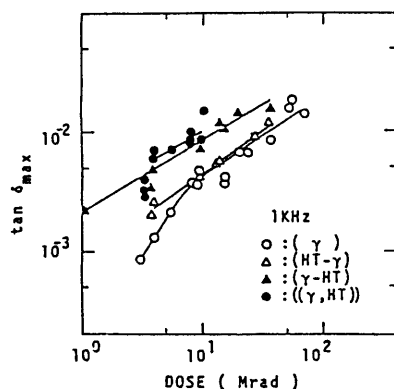


Fig. 6 Irradiation dose dependence of $\tan \delta_{max}$.

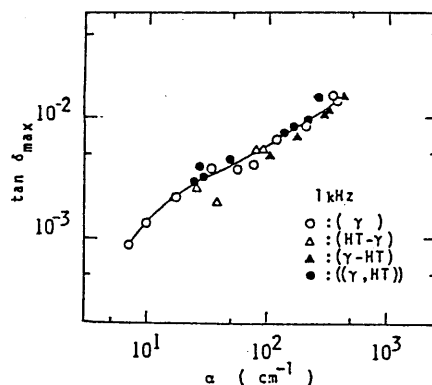


Fig. 7 Maximum dielectric loss tangent, $\tan \delta_{max}$, as a function of α .

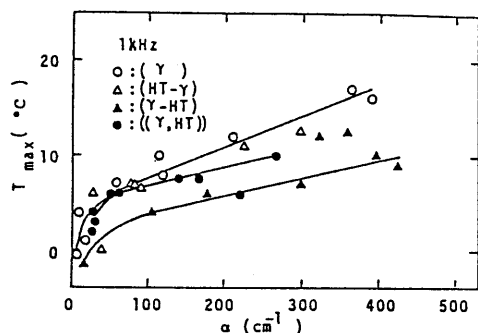


Fig. 8 Temperature appearing $\tan \delta_{\max}$, T_{\max} , as a function of α .

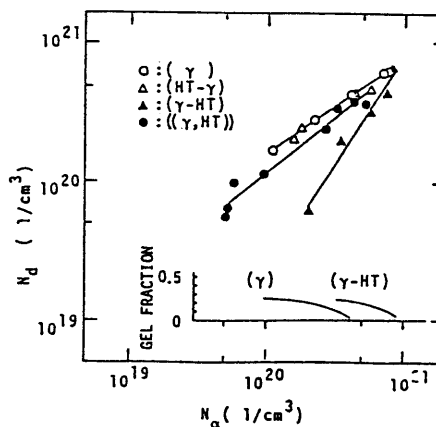


Fig. 9 Dipole density N_d , contributing to the primary dispersion vs. density of carbonyl groups N_α , estimated from α .

are replotted in Fig. 7 as a function of absorption coefficient α of carbonyl groups. Although a difference of $\tan \delta_{\max}$ among variously treated samples becomes less clear than in Fig. 6, it can be seen from Fig. 7 that the $(\gamma\text{-HT})$ sample shows a slightly lower $\tan \delta_{\max}$ than the others when α is beyond 100 cm^{-1} . The details shall be discussed later in terms of gel fraction, chain scission and cross linking.

The temperature, T_{\max} , where a maximum of $\tan \delta$ on the 1 kHz curve appears, is shown in Fig. 8 as a function of α . In all cases the value of T_{\max} shifts to higher temperatures with incremental α . The (γ) sample shows the highest value of T_{\max} and, on the other hand, the $(\gamma\text{-HT})$ sample shows the lowest value of T_{\max} at $\alpha = 200\text{ cm}^{-1}$. The $(\text{HT-}\gamma)$ and $((\gamma, \text{HT}))$ samples show the middle value of T_{\max} between those for the (γ) and $(\gamma\text{-HT})$ samples. A close look reveals that the temperature of T_{\max} of the $(\text{HT-}\gamma)$ sample is higher than that of the $((\gamma, \text{HT}))$ sample and is close to that of the (γ) sample.

Figure 9 shows the dipole density N_d , contributing to the primary dispersion, versus density of carbonyl groups N_α estimated from the absorption coefficient for variously treated samples. The density of dipole N_d , which related to the primary dispersion, can be estimated using Onsager's equation as

$$\epsilon_{r0} - \epsilon_{r\infty} = \frac{3\epsilon_{r0}}{2\epsilon_{r0} + \epsilon_{r\infty}} \times \left(\frac{\epsilon_{r\infty} + 2}{3} \right)^2 \times \frac{N_d \mu_0^2}{3\epsilon_0 kT}, \quad (1)$$

where k is the Boltzmann constant, μ_0 the dipole moment (assumed to be 2.3 Debye), ϵ_0 the permittivity of free space. The value of T was chosen to be 90°C so as to be lowest temperature below which the relaxation of primary dispersion indicated in Figs. 5(a) and (b) could be considered complete. Therefore, the value of ϵ_r' , at 90°C for the 40 Hz curve on the dielectric properties was applied to ϵ_{r0} which is the relaxed relative permittivity.

The value of $\epsilon_{r\infty}$ at 90 °C was estimated using eq. (2).

$$\epsilon_{r\infty} = 2.2 + \frac{(\epsilon_r'(-90\text{ °C}) - 2.2) \times (273 - 90)}{(273 + 90)}, \quad \text{-----}(2)$$

where a part of $\epsilon_{r\infty}$ at -90 °C was assumed to be 2.2, due to electronic and atomic polarizations, and the relaxation which occurs at a lower temperature (usually denoted as γ relaxation) than that for the primary dispersion, was also assumed to be obeyed the Debye's equation. The apparent contribution at -90 °C was estimated as $\epsilon_r'(-90\text{ °C}) - 2.2$.

On the other hand, the axis of abscissa in Fig. 9 is the density of carbonyl groups $N\alpha$, estimated using eq. (3) at the absorption band of 1715 cm^{-1} on the IR spectrum.

$$\alpha = (-1/d) \cdot \ln(I/I_0) = \epsilon \cdot C = (\epsilon N\alpha / N_A) \times 10^3 \quad \text{-----}(3)$$

where α is the absorption coefficient, d the film thickness, I_0 and I the incident and transmitted light intensities, ϵ the molar absorption (extinction) coefficient (assumed to be 300 (mol/l cm^{-1})), C the molarity, N_A Avogadro's number $6.02 \times 10^{23} \text{ mol}^{-1}$, respectively. As a matter of fact, the value of $N\alpha$ contains both contributions from carbonyl groups in the amorphous region and at the surface of crystal. Each sample shows a linear relationship of $N\alpha \propto N\alpha^n$. The values of n are 0.71 for the (γ) and (HT- γ) samples, 1.15 for the ((γ , HT)) sample and 1.55 for the (γ -HT) sample, respectively. From the comparison of $N\alpha$ for each sample at $N\alpha = 3 \times 10^{20} \text{ cm}^{-3}$, the (γ) and (HT- γ) samples show the largest value of $N\alpha$, the ((γ , HT)) sample is the next, and the (γ -HT) sample shows the smallest one. The inset in Fig. 9 will be discussed later.

3.3 Gel Fraction

Figures 10(a) and (b) show gel fraction as functions of irradiation dose and absorption coefficient of carbonyl groups for the (γ), (γ -HT), and ((γ , HT)) samples, respectively. The gel fraction for the non-irradiated sample

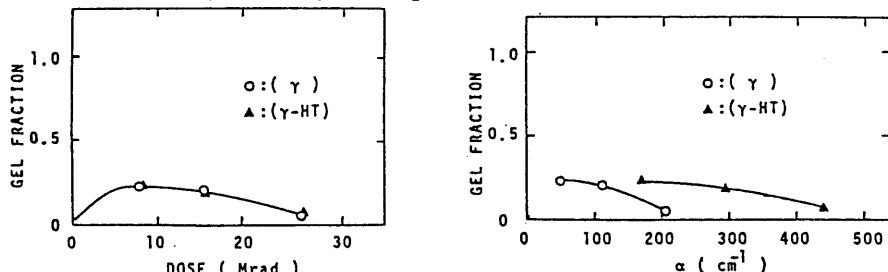


Fig. 10 Gel fraction as functions of irradiation dose and absorption coefficient α .

was almost undetectable. The gel fractions for the (γ) and (γ -HT) samples once showed an increase and then a decrease with increasing irradiation dose, as seen from Fig. 10(a). From Figs. 10(a) and (b), it can be seen that the value of α for the (γ) sample rapidly increases by thermal aging subsequent to γ -irradiation, but *the gel fraction does not change by thermal aging and is determined only by γ -irradiation.*

4. Discussion

4.1 Phenomenological Discussion of Oxidative Degradation

It has been found that irradiation exposure on PE produces intermediates such as oxidation products, unsaturated compounds, hydroperoxides and residual free radicals which turn into carbonyl groups upon thermal heating.¹¹⁻¹³⁾ It can be suggested that such intermediates can contribute to a rapid increment of α for the (γ) sample at the beginning of thermal aging. To proceed the discussion, we assume the following oxidative degradation process as shown in Fig. 11; and also that the processes due to thermal aging

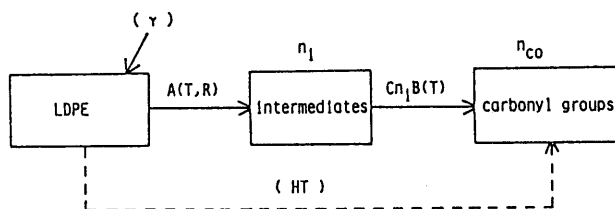


Fig. 11 Scheme for degradation by thermal aging and irradiation.

and irradiation exposure proceed independently of each other. The intermediates of n_1 $1/cm^3$ are produced at a rate of $A = A(R, T)$ per unit time, where R is irradiation dose rate and T is the temperature ($^{\circ}C$). The value of A is denoted at room temperature as

$$A = A(R, T) = A_{20} \quad (T = 20^{\circ}C). \quad \text{-----}(4)$$

In following discussions it is assumed that the intermediates finally turn into carbonyl groups. If one of the intermediates results in the number of carbonyl groups c , the number of n_1 of the intermediates produces the number of cBn_1 of carbonyl groups, where the constant B is assumed to depend only on temperature. The value of B is denoted as

$$B = B(T) = B_{20} \quad \text{-----}(5)$$

at $20^{\circ}C$. We can express $dn_1(t_r)/dt_r$ and $dn_{co}(t_r)/dt_r$ during irradiation exposure as

$$dn_1(t_r)/dt_r = A_{20} - B_{20}n_1(t_r) \quad \text{-----}(6)$$

and

$$dn_{c0}(t_r)/dt_r = cB_{20}n_1(t_r) \quad \text{-----}(7)$$

respectively, when n_{c0} is the number of carbonyl groups. Using the initial conditions at $t_r = 0$, which are $n_1(0) = n_{c0}(0) = 0$, we can get the following equations.

$$n_1(t_r) = (A_{20}/B_{20}) \cdot (1 - \exp(-B_{20}t_r)) \quad \text{-----}(8)$$

$$n_{c0}(t_r) = cA_{20}(t_r + (1/B_{20}) \cdot \exp(-B_{20}t_r) - 1/B_{20}) \quad \text{-----}(9)$$

Equations (8) and (9) represent the numbers of intermediates n_1 and carbonyl groups n_{c0} , respectively.

After irradiation, the intermediates n_1 change into carbonyl groups by thermal aging. The increment Δn_{c0} due to n_1 depends on t_{HT} . We assume that the change can be written as

$$d\Delta n_{c0}(t_{HT})/dt_{HT} = K \cdot (cn_1(t_r) - \Delta n_{c0}(t_{HT})), \quad \text{-----}(10)$$

where the constant K is assumed to be independent of irradiation dose and to depend on T as $K = K(T)$. The value of $K(T)$ coincides with that of $B(T)$ at 90 °C, namely

$$K(T) = B(T) = B_{90} \quad (90 \text{ } ^\circ\text{C}), \quad \text{-----}(11)$$

If $\Delta n_{c0}(0) = 0$ in eq. (10), we obtain the following equation.

$$\Delta n_{c0}(t_{HT}) = cn_1(t_r) \cdot (1 - \exp(-B_{20}t_{HT})) \quad \text{-----}(12)$$

Since we have arranged the results shown in Figs. 1-4 by using the absorption coefficient α of carbonyl groups, we must change the dimension of eqs. (8), (9), and (12) into those of α . When we assume that the value of n_{c0} is in proportion to α with a constant c_0 , we obtain the following constant

$$c_0 = c_0' c_0'' / N_A \quad \text{-----}(13)$$

where N_A is Avogadro's number, α' the molecular absorption coefficient of carbonyl groups. The values of n_1 , α_0 and $\Delta \alpha_0$ can be transferred into α_1 , α_r , and $\Delta \alpha_{INT}$, respectively, as follows.

$$\alpha_1(t_r) = \alpha_0 n_1 = (A_{20}/B_{20}) \cdot (1 - \exp(-B_{20} t_r)), \quad \text{----(14)}$$

$$\alpha_r(t_r) = \alpha_0 \alpha_0 = A_{20}' \cdot (t_r - (1/B_{20}) \cdot \exp(-B_{20} t_r) - 1/B_{20}), \quad \text{--(15)}$$

and

$$\begin{aligned} \Delta \alpha_{INT}(t_{HT}) &= \alpha_0 \Delta \alpha_0 \\ &= (A_{20}'/B_{20}) \cdot (1 - \exp(-B_{20} t_r)) \cdot (1 - \exp(-B_{20} t_{HT})) \\ &= \alpha_1(t_r) \cdot (1 - \exp(-B_{20} t_{HT})), \end{aligned} \quad \text{-----(16)}$$

where $A_{20}' = \alpha_0 A_{20}$. -----(17)

When irradiated at 90 °C, the value of A is written as A_{90} . Although the value of $\alpha_1(t_r)$ can't be observed by the infrared absorption, the number of n_1 has been discussed in the dimension of α . The value of $\Delta \alpha_{INT}$ in eq. (16) refers to the increment of oxidative products due to intermediates during thermal aging which are produced by irradiation for t_r at room temperature. Therefore, $\Delta \alpha_{INT} = \alpha_1$ when t_{HT} tends to infinity.

The values of A_{20}' , B_{20} and B_{90} can be obtained by applying eqs. (14)-(16) to the results of the (γ) and (γ -HT) samples. Equation (16) corresponds to the $\Delta \alpha - \Delta t_{HT}$ curves in Fig. 4, $t_{HT} = \Delta t_{HT}$ as mentioned

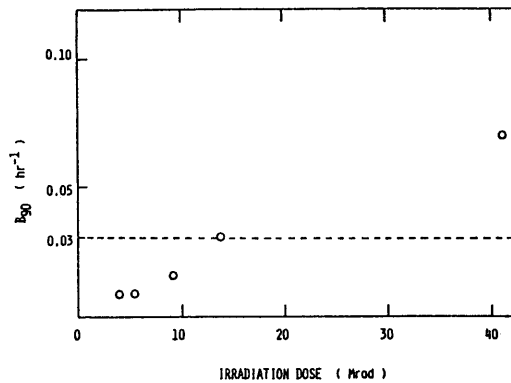


Fig. 12 Variation of $B(T) = B_{90}$ with irradiation dose.

before. From the equation of

$$\Delta \alpha_{\text{INT}} \propto (1 - \exp(-B_{90} t_{\text{HT}})) \quad \text{-----}(18)$$

Though the values of B_{90} show an increasing trend with irradiation dose as shown in Fig. 12, we estimated it as

$$B_{90} = 0.03 \text{ h}^{-1}, \quad \text{-----}(19)$$

which is chosen such as to being close to the numerical average. The details of the value will be discussed in 4.2. The value of m_1 can be obtained from $\alpha_1 = \Delta \alpha_{\text{INT}}(\infty)$ by extrapolating t_{HT} to ∞ . These results are shown in Fig. 13. The value of α for the (γ) samples in Fig. 1 corresponds to α_r . The parameters A_{20}' and B_{20} in eqs. (14) and (15) can be estimated as

$$A_{20}' = 0.745 \quad \text{cm}^{-1} \cdot \text{h}^{-1} \quad \text{-----}(20)$$

$$B_{20} = 3.73 \times 10^{-3} \quad \text{h}^{-1}$$

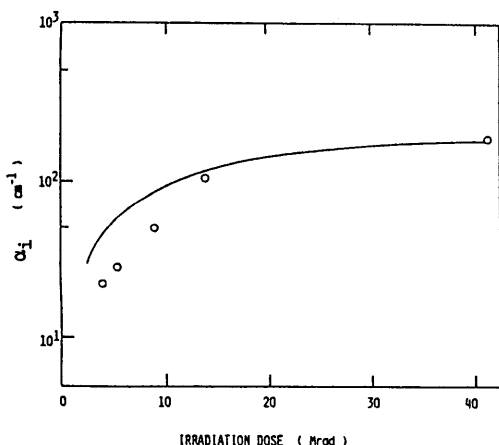


Fig. 13 Absorption coefficient α_1 of carbonyl groups due to intermediates produced by irradiation.

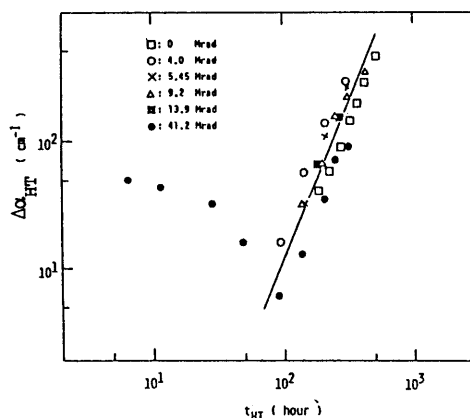


Fig. 14 Change of $\Delta \alpha_{\text{HT}}$ by pure thermal aging for (γ -HT) and (HT) samples as a function of t_{HT} .

by curve-fitting $\alpha_r(t_r)$ in Fig. 1 and $\alpha_1(t_r)$ in Fig. 13. The solid lines for the (γ) sample in Fig. 1 and for α_1 in Fig. 13 are drawn using the above values of A_{20}' and B_{20} .

Next, we shall discuss about the (γ -HT) and the (HT- γ) samples. The thermal oxidative degradation $\Delta \alpha_{\text{HT}}$ can be estimated from the results for the (γ -HT) sample. Since the value of α shown in Fig. 3 is a total value of α_r , $\Delta \alpha_{\text{INT}}$ and $\Delta \alpha_{\text{HT}}$, the value of $\Delta \alpha_{\text{HT}}$ due to thermal oxidation can be expressed as

$$\Delta \alpha_{\text{HT}}(t_{\text{HT}}) = \alpha(t_{\text{HT}}) - \alpha_r - \Delta \alpha_{\text{INT}}(t_{\text{HT}}) \quad \text{-----}(21)$$

Figure 14 shows the relation between $\Delta \alpha$ and t_{HT} for the (γ -HT) sample. In the figure, the value of α for the (HT) samples is presented as $\Delta \alpha_{HT}$ for reference. The values of $\Delta \alpha_{HT}$ for each sample increase with t_{HT} , and there is no systematic change according to irradiation dose. The (γ -HT) sample irradiated with 41.2 Mrad shows a strange value of $\Delta \alpha_{HT}$ below $t_{HT} = 90$ h. This may be due to error introduced in calculation using eq.(11), and the reason should be considered further. From the results of Fig. 14, the relation between $\Delta \alpha_{HT}(t_{HT})$ and t_{HT} can be expressed as

$$\Delta \alpha_{HT} = \beta \cdot t_{HT}^n. \quad \text{-----}(22)$$

The values of β and n are evaluated as $1.69 \times 10^{-4} \text{ cm}^{-1} \cdot \text{h}^{-n}$ and 2.44, respectively. The solid lines in Figs. 1 and 2 for the (γ -HT) sample are drawn based upon the following equation using the above values of A_{20}' , B_{20} , β , and n .

$$\alpha = \alpha_r + \Delta \alpha_{INT} + \Delta \alpha_{HT} \quad \text{-----}(23)$$

On the other hand, the solid line for the (HT- γ) sample in Fig. 1 is drawn by using the following equation,

$$\alpha = \Delta \alpha_{HT} + \alpha_r. \quad \text{-----}(24)$$

Finally, we shall discuss the ((γ , HT)) samples. It can be considered that the oxidative degradation mechanism for the ((γ , HT)) samples is essentially similar to that of the (γ) samples. As the thermal oxidation takes place with the irradiation exposure at 90 °C, the value of α for the ((γ , HT)) samples is expressed as

$$\alpha = A_{90}'(tr + (1/B_{90}) \cdot \exp(-B_{90} tr) - (1/B_{90})) + \beta t_{HT}^n, \quad \text{-----}(25)$$

where A_{90}' corresponds to the value for $\infty c A_{90}$. The value of A_{90}' can be obtained from curve-fitting the results for the ((γ , HT)) samples as shown by the solid line in Fig. 1. The evaluated value of A_{90}' is

$$A_{90}' = 1.7 \times A_{20}' = 1.27 \text{ cm}^{-1} \cdot \text{h}^{-1}. \quad \text{-----}(26)$$

The fitted lines for the (γ -HT) and the (HT- γ) samples in Fig. 1 deviate from the results for irradiation exposure below 10 Mrad. The experimental results for the (γ -HT) sample are larger than the one obtained using the experimental formula. On the other hand, for the (HT- γ) sample the contrary is true. However, the experimental results in Figs. 1 and 2 and the calculated results coincide with each other beyond 10 Mrad.

4.2 Discussion of Intermediates

We shall discuss substantially about the intermediates. There have been many papers written about the chemical and structural changes of PE during and after irradiation. The irradiation of PE in vacuo makes alkyl radicals having a life time of one day at room temperature, allyl radicals having a life time of several months, and polyenyl radicals which appear beyond radiation dose of several thousand Mrad and are very stable.¹¹⁾ By introducing air after irradiation in vacuo, allyl radicals react with oxygen and become peroxide radicals which give asymmetric ESR signal. These peroxide radicals change into carbonyl groups via hydroperoxide radicals and into aldehyde groups via chain scission.¹¹⁾ The above reactions can be considered to occur simultaneously. If irradiation exposure is the last on the sample treatment such as the (γ) or the (HT- γ) samples, an asymmetric singlet spectrum on ESR is observed.⁷⁾ It has been considered that it is composed of allyl, peroxide and polyenyl radicals. Moreover, it has been reported that unsaturated compounds contribute to the formation of carbonyl groups.^{12,13)} Therefore, these residual free radicals and unsaturated compounds producing during the irradiation exposure are considered as intermediates.

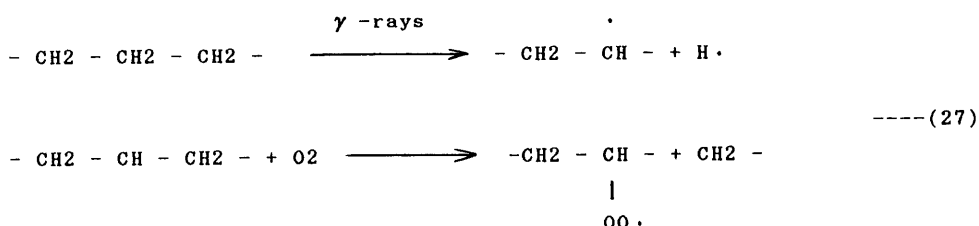
As mentioned in 4.1, the inverse of $K(T) = B_{90}$ indicates the time constant needed to change the intermediates into carbonyl groups. We have assumed that the value of $K(T)$ does not change with irradiation dose. However, with increasing irradiation dose the value of B_{90} tends to increase as shown in Fig. 12. Generally, it has been said that chain scission is the preferred mechanism over crosslinking during irradiation of PE in air. This indicates that the value of B_{90} for the ((γ , HT)) samples change with irradiation. Therefore, this should be discussed in the future.

4.3 Degradation of Dielectric Properties

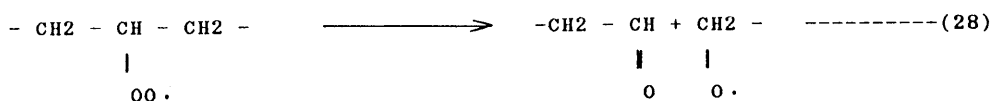
First, we shall discuss a shift of T_{\max} with increasing α and the difference of T_{\max} among the samples. As one of reasons for the shift of T_{\max} , it can be considered that an increase of intermolecular force occurs, either to dipole-dipole interaction or crosslinking of molecular chains. In the case of the (γ) sample, the gel fraction increases with increasing radiation dose, but it decreased when the radiation dose became > 10 Mrad. However, T_{\max} shifted to higher temperatures even if the radiation dose is > 10 Mrad. Therefore, it seems to be difficult to explain the change in T_{\max} with α in terms of structural change due to crosslinking and/or chain scission. As a candidate for the reason, it can be considered that the intermolecular force between dipoles increases with the number of carbonyl groups in an amorphous region.

The (γ -HT) sample shows a lower value of T_{\max} than the (γ) sample. From Fig. 10(a), the gel fraction was determined almost by a radiation dose. The value of α increased after HT treatment subsequent to γ -irradiation, and the gel fraction did not change. However, the (γ -HT) sample shows larger value of gel fraction than the (γ) sample at the same value of α as seen

from Fig. 10(b). Moreover, the number of dipoles will be expected to be the same for both samples when their α values are equal. It can be considered that the chain scission in an amorphous region for the (γ) sample takes place without gelatinization during further HT treatment. This chain scission process shall be described as follows: when γ -irradiation is applied to LDPE, the following reactions presented in eq. (27) will take place.^{11,14)}



Then the following chain scission reaction takes place by thermal aging subsequent to γ -irradiation.



From the above discussion, it has been explained why the value of T_{\max} of the (γ -HT) sample is lower than that of the (γ) sample.

The ((γ ,HT)) and (HT- γ) samples show the middle value of T_{\max} between both the (γ) and (γ -HT) samples. Although the gel fraction for the ((γ ,HT)) and (HT- γ) samples are not yet obtained, the dependence of T_{\max} on oxidation for them also may be explained in terms of crosslinking, chain scission and dipole-dipole interaction.

Now, we shall discuss the results of (γ) and (γ -HT) shown in Fig. 9. The inset in Fig. 9 shows the gel fraction as a function of $N\alpha$. In the range of $N\alpha$ from 3×10^{20} to $9 \times 10^{20} \text{ cm}^{-3}$, the (γ -HT) sample shows a larger value of the gel fraction than the (γ) sample at the same value of $N\alpha$. On the other hand, the value of $N\alpha$ for the (γ) sample is larger than that for the (γ -HT) sample when their $N\alpha$ values are the same. This seems to be due to a smaller contribution of carbonyl groups to the primary relaxation for the (γ -HT) sample because of its larger gel fraction. However, the gel fraction of (γ -HT) sample seems to coincide with that of (γ) sample when an irradiation dose increases as seen from Figs. 10(a) and (b).

Because oxidation by thermal aging for the (HT- γ) sample can be almost negligible,^{8,15)} it can be considered that the gel fraction of (HT- γ) sample is the same as that of the (γ) sample. Therefore, the $N\alpha$ vs. $N\alpha$ characteristics for the (HT- γ) have shown the same trend to that for the (γ) sample.

5. Conclusions

A 25 μ m thick low density polyethylene film free from additives has been subjected to γ -irradiation with a dose rate of $5.02 \times 10^4 - 5.3 \times 10^4$ rad/h at room temperature in air (denoted as γ) and/ or thermal aging at 90 °C in air (denoted as HT). These γ and HT treatments have been carried out by single, sequential, and simultaneous applications. Oxidative degradation and degradation of dielectric properties have been discussed with respect to the absorption coefficient α of carbonyl group and change in structure. The results are as follows.

The order of oxidative degradation is $(\gamma) \leq (\text{HT}-\gamma) < (\gamma-\text{HT}) \leq ((\gamma, \text{HT}))$, where $()$ means the single, or sequential application of γ and HT, the bar means the order of the application of the treatments and $((\gamma, \text{HT}))$ means the simultaneous application of γ and HT. In case of $t_{\text{HT}} = t_r$, the oxidative degradation is almost same for $(\gamma-\text{HT})$ and $((\gamma, \text{HT}))$.

It has been suggested that the $(\text{HT}-\gamma)$ and $(\gamma-\text{HT})$ samples differ with oxidative degradation by the order of application of (HT) and (γ) . The latter samples show larger degradation.

It is concluded that the difference in degree of oxidative degradation between the $(\text{HT}-\gamma)$ and the $(\gamma-\text{HT})$ samples is due to the intermediates such as residual free radicals, unsaturated compounds and hydroperoxides produced by γ irradiation in air which turn into carbonyl groups by thermal aging.

Experimental formulae for oxidative degradation of polyethylene by combination of thermal aging and γ -irradiation have been derived by taking the intermediates into account.

We have also discussed the dielectric properties of (γ) , $(\text{HT}-\gamma)$, $(\gamma-\text{HT})$, and $((\gamma, \text{HT}))$ samples. The (γ) sample shows the highest temperature of primary relaxation T_{max} among the samples tested and the value of T_{max} shifts to higher temperatures with oxidation. This is explained in terms of an increase of dipole-dipole interaction. Also, the value of T_{max} for the $(\gamma-\text{HT})$ sample shifts to higher temperatures with oxidation, similar to the (γ) sample, and is the lowest temperature among the other samples. The difference of T_{max} between the (γ) and $(\gamma-\text{HT})$ samples is explained in terms of chain scission due to thermal heating. The values of T_{max} for the $(\text{HT}-\gamma)$ and $((\gamma, \text{HT}))$ samples lie between the temperatures of the (γ) and $(\gamma-\text{HT})$ samples. This seems to depend on the balance among the dipole-dipole interaction, the chain scission and crosslinking. It has been shown that the number of dipoles N_d , contributing to the primary dispersion, depends on the gel fraction. The order of N_d , estimated from Onsager's equation, is as $(\gamma) \geq (\text{HT}-\gamma) \geq ((\gamma, \text{HT})) \geq (\gamma-\text{HT})$ samples.

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