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Thermally stimulated current study in γ-ray irradiated low density polyethylene

Ki-Yup Kim [a], Boo-Hyung Ryu [b], Doo-Jin Byun [c], Sei-Moon Shin [c,*]

[a] *Radiation Application Team, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejon 305-600, South Korea*
[b] *Safety Engineering Department, Dongguk University, Kyungju 780-714, South Korea*
[c] *Material Testing Laboratory, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-600, South Korea*

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Abstract

Thermally stimulated current and relaxation map analysis (RMA) were used to characterize the low temperature transition of low density polyethylene (LDPE). Four current peaks were observed. The peaks at about −125°C, −25°C, and 90°C are indications of the γ-, β-, α-transition, respectively, and a new, formerly unknown peak at about 50°C will be attributed to the space charge relaxation. The RMA data showed that compensation temperature (T_c) and degree of disorder increased with increasing the γ-ray intensity and decreasing antioxidant content, whereas the compensation time (τ_c) decreased. It can be concluded that the cooperative molecular motion in LDPE system becomes more active as the γ-ray intensity increases and antioxidant content decreases. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermally stimulated current; Relaxation map analysis; Low density polyethylene

1. Introduction

Low density polyethylene (LDPE) is one of the most widely studied polymers because it has the simplest chemical structure. Especially, LDPE has been widely used as insulating materials for power cables and communication cables because of good electrical properties. On the other hand, when used as insulators are exposed to the radiant rays and the corona discharge, it oxidizes to a greater or lesser degree and its insulating ability deteriorates.

Measurements of the electrical conduction in oxidized LDPE have shown that oxidation products such as carbonyl groups act as deep traps and carrier mobilities decrease [1,2]. The oxidation of LDPE is a practically important form of degradation. The method to measure the degradation of cable insulation has recently been extended to predicting cable breakdown and various test methods such as the direct current high voltage test, the dielectric dissipation factor test, and the partial discharge test are in use for this purpose.

In this paper, the effect of the γ-ray dose and the antioxidant content of LDPE have been studied by using thermally stimulated current (TSC) and relaxation map analysis (RMA). TSC and RMA studies were based on the single Debye relaxation theory by Bucci [3] and Arrhenius equation [4,5].

2. Experimental

LDPE (Han Hwa Chemical Co., LDPE 830, MI 2.0, density 0.923 g/cm^3), crosslinking agent, dicumyl peroxide (DCP, Tokyo Kasei Organic Chemicals) and antioxidant, butylated hydroxytoluene (BHT, Aldrich Chemicals), which have chemical structures shown in Fig. 1, were used in this study.

LDPE and antioxidant (0.1–0.4 wt part) were mixed with roll mixer at 120°C for 30 min, and then DCP (2 wt parts) was mixed into the mixture for 5 min. Out of LDPE mixture specimens were made by crosslinking in

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[*] Corresponding author.

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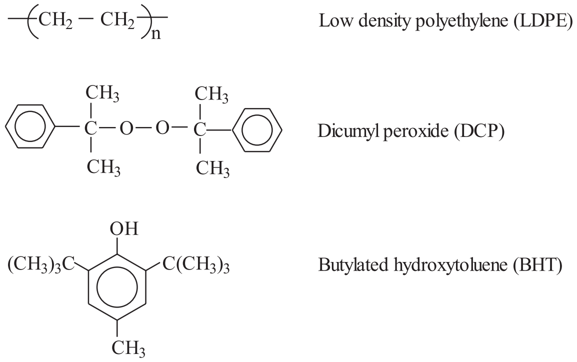

Fig. 1. Chemical structures of materials used in this study.

press (250 kg/cm^2) at 175°C for 15 min and then irradiated by different doses of γ-radiation (0–100 Mrad) at the rate of 0.5 Mrad/h at room temperature in air. The resin formulations used in this study are described in Table 1.

TSC measurements were carried out by polarizing the sample at 80°C and −10°C with a polarization voltage of 1200 V/mm using TSC/RMA 91000 (Solomat Co.). The heating rate was 7°C/min and the sample thickness was 0.01–0.1 mm. Dust and moisture in tested samples were removed under vacuum (at 10^{-4} mbar for 24 h) prior to the test. RMA measurements were carried out as follows. The sample was polarized at 1200 V/mm for 20 min (the polarization time, t_p) and cooled rapidly to the temperature, which was 5°C lower than the polarization temperature (T_p) and then the polarization voltage (E_p) was removed. The sample was held at that temperature for another 2 min and rapidly cooled again to the temperature that was 30°C lower than T_p by 20°C/min and finally heated to a temperature that was higher than T_p at a heating rate of 7°C/min.

Table 1
Details of LDPE formulations used

Code	γ-ray dose (Mrad)	BHT content (wt part)
LPE	0	0.2
LPE-20	20	0.2
LPE-40	40	0.2
LPE-60	60	0.2
LPE-80	80	0.2
LPE-100	100	0.2
FPE-1	40	0.1
FPE-2	40	0.2
FPE-3	40	0.3
FPE-4	40	0.4
EPE-1	80	0.1
EPE-2	80	0.2
EPE-3	80	0.3
EPE-4	80	0.4

3. Results and discussion

TSC spectra as a function of the γ-ray dose are shown in Figs. 2 and 3. Two transition peaks at around −125°C and −25°C in the low temperature range (−150°C to 10°C) can be seen in Fig. 2. The intensity and area of both TSC peaks increase with increasing the γ-ray dose. It is believed to be due to the increase of the carbonyl group content by LDPE degradation. The first peak is related to the γ-transition peak resulted from the local motion of LDPE chain and the second peak is to be due to the β-transition associated with carbonyl group [6–8].

TSC spectra in the high temperature range (10–100°C) are shown as a function of the γ-ray dose in Fig. 3. Two

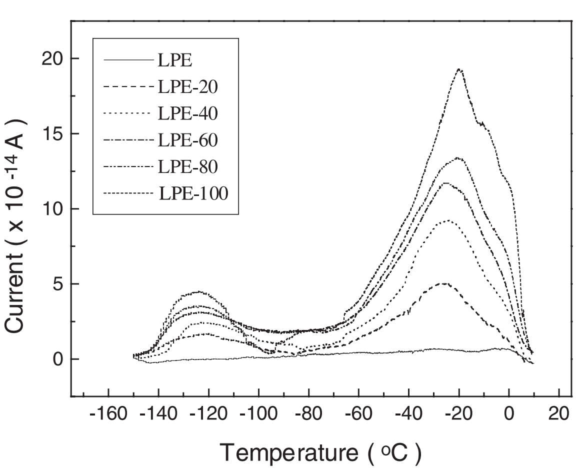

Fig. 2. TSC spectra of LDPE with different dose of the γ-ray at −150°C to 10°C: testing conditions; $T_p = 80°C$, $E_p = 1200$ V/mm and $t_p = 20$ min.

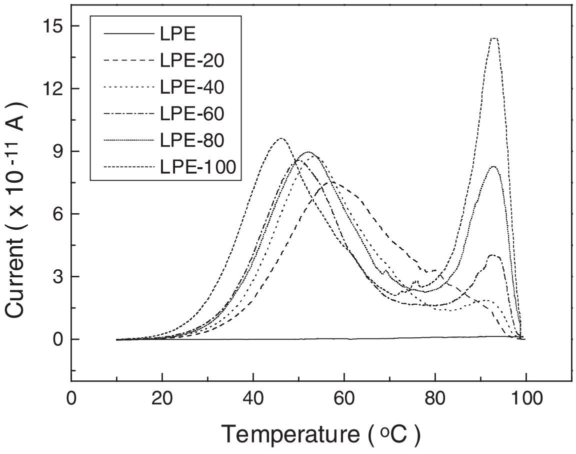

Fig. 3. TSC spectra of LDPE with different dose of the γ-ray at 10–100°C: testing conditions; $T_p = 80°C$, $E_p = 1200$ V/mm and $t_p = 20$ min.

transition peaks at around 50°C and 90°C can be seen from the Fig. 3. The α-transition of LDPE is located at around 90°C and a new unknown peak observed at around 50°C is to be due to the space charge [6].

TSC spectra as a function of the antioxidant (BHT) content at 40 and 80 Mrad are shown in Figs. 4 and 5. The intensity and area of both TSC peaks decreased with increasing the antioxidant amount. It is believed to be due to the decrease of the carbonyl group content. As explained above, the γ- and β-transition peak of LDPE at −130°C and −25°C were observed.

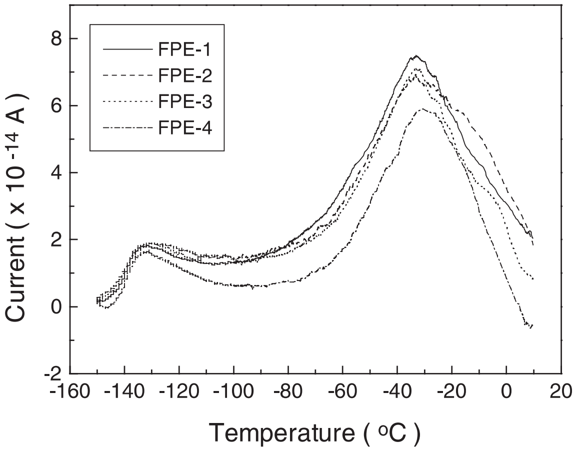

Fig. 4. TSC spectra of LDPE with different content of the antioxidant (BHT) at 40 Mrad: testing conditions; $T_p = -10$°C, $E_p = 1200$ V/mm and $t_p = 20$ min.

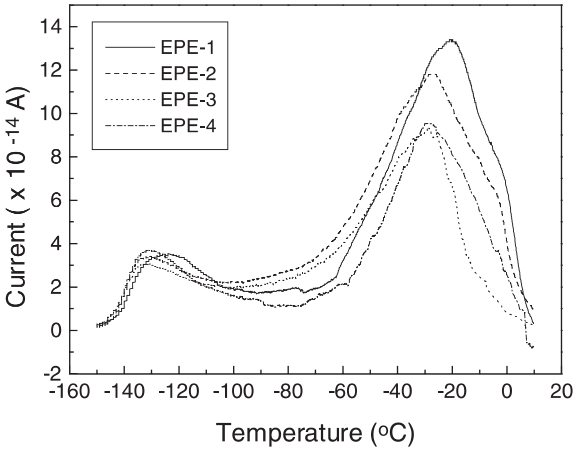

Fig. 5. TSC spectra of LDPE with different content of the antioxidant (BHT) at 80 Mrad: testing conditions; $T_p = -10$°C, $E_p = 1200$ V/mm and $t_p = 20$ min.

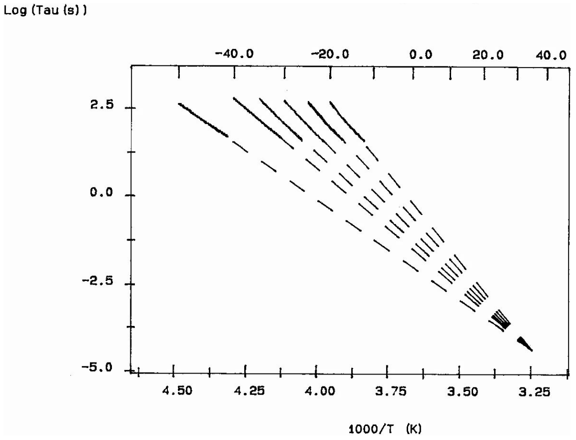

Fig. 6. Plot of the compensation search for RMA data of LPE-40; $T_p = -50$°C to −20°C.

More detailed results were obtained from the RMA measurements [9–14], that were performed for the β-transition region. As an illustrating example, the relaxation map for the sample LPE-40 is shown in Fig. 6. If several Arrhenius lines converge into a single point, as seen in the figure, this point is called a compensation point. The compensation point is related to the characteristics of the amorphous regions of amorphous or semi-crystalline polymer. From the analysis of this relaxation map we can derive the activation enthalpy (ΔH) and entropy (ΔS). The degree of disorder (DOD) is defined in Ref. [15] using the activation entropy value $\Delta S_{0,\mathrm{h}}$ extrapolated to $\Delta H = 0$ and expressed in units (cal/K mol) by the relation

$$\mathrm{DOD} = 100 + \Delta S_{0,\mathrm{h}} \tag{1}$$

where an arbitrarily selected additive constant is introduced to make the DOD value positive. The DOD value has also been found in Ref. [14] to characterize the influence of compatibility and thermal stress in polymer blends.

The data of the compensation temperature (T_c), the relaxation time (τ_c) and DOD, obtained by the compensation search, are presented in Tables 2 and 3. The increase in the γ-ray dose of LDPE caused the increase in the T_c values. The compensation temperature is related to the maximum number of cooperative movement; a high T_c value means more cooperative segmental motion [13,14]. Consequently, the segmental motion is more active as the γ-ray dose increase. On the other hand, the increase of the γ-ray dose indicates the decrease of relaxation time. The trend observed here is believed to be due to the cooperative effect of carbonyl group having polar groups. The value of DOD is increased with increasing of the γ-ray dose. This tendency is also considered to be due to the increase of carbonyl group by degradation.

RMA data as a function of the BHT content at 40 and 80 Mrad is shown in Table 3. The increase of BHT content causes the decrease of the T_c and DOD. As

Table 2
RMA data of LDPE systems with different γ-ray doses

Sample	T_c (°C)	log τ_c (s)	DOD (cal/K mol)
LPE	–	–	–
LPE-20	27.31	−3.58	57.83
LPE-40	28.69	−3.79	58.79
LPE-60	30.77	−3.89	59.24
LPE-80	32.79	−4.27	60.94
LPE-100	34.56	−4.51	62.06

Table 3
RMA data of LDPE systems with different BHT content

Sample	T_c (°C)	log τ_c (s)	DOD (cal/K mol)
40 Mrad			
FPE-1	31.12	−4.13	60.31
FPE-2	28.69	−3.79	58.79
FPE-3	28.37	−3.36	56.83
FPE-4	26.33	−3.19	56.04
80 Mrad			
EPE-1	34.91	−4.34	61.27
EPE-2	32.79	−4.27	60.94
EPE-3	30.46	−4.05	50.98
EPE-4	28.72	−3.90	59.27

explained above, the decrease of the T_c and DOD has a consequence the decrease of the cooperative segmental motion. In addition, the increase of BHT content indicates the increase of τ_c. T_c and DOD values of LDPE systems at 80 Mrad are much larger than those of LDPE systems at 40 Mrad. On the other hand, τ_c of LDPE systems at 80 Mrad is much smaller that of LDPE systems at 40 Mrad. The trend observed here is believed to be due to the increase of carbonyl group by degradation.

4. Conclusions

The intensity and the area of TSC peak were increased as the γ-ray dose was increased and BHT content was decreased. As the γ-ray dose increased and BHT content decreased, the compensation temperature and DOD increased, while relaxation time decreased. The unknown peak at around 50°C was to be due to the space charge. The critical temperature and DOD values of LDPE systems at 80 Mrad were much larger than those of LDPE systems at 40 Mrad, while relaxation time was much smaller. From RMA data, we could conclude that the segmental motion was more active with increasing the γ-ray dose and decreasing BHT content.

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