

On the Temperature Characteristics and Electrical Conduction of Irradiated Low Density Polyethylene

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Abstract

This paper attempted to investigate the temperature characteristics and electrical conduction when low density polyethylene is irradiated. It was found that the $\log \rho$ versus $1/T$ in irradiated polyethylene specimen resulted in different characteristics when it was heated upto above the melting point from when it was heated at the beginning stage. It was also found that the relation between the temperature and volume resistivity represented jumping phenomenon and that crystallization by thermal change was closely related to the fusion of crystalline region.

요 약

照射된 低密度 polyethylene 의 전기전도도와 온도특성을 중심으로 하여 조사해 보았다. 照射 polyethylene 시료에 대해서는 融點 이상까지 昇溫시켜 보던 가열 후의 $\log \rho - \frac{1}{T}$ 특성은 처음 가열과정에서 얻은 결과와는 전혀 다른 특성이 생겼으며 온도와 體積抵抗率과의 관계에서는 跳躍現象이 나타나고 온도에 의한 결정화도의 변화가 결정영역의 용해와 밀접한 관계가 있음을 究明하였다.

I. Introduction

Many valuable researches¹⁻²⁾ and experiments have been made after the report on the improved high polymer by irradiation of radiation as an organic insulation material; however, the phenomenon of electric conduction known as the basic electron process has still remained as unclear. Some have

suggested that most of high polymer could be explained as a phenomenon of ionic conduction, but in reality, it was not at all clear what the ions are composed of as charge carriers.

The electric conduction in an insulation material has generally been considered as the result of the absorption and decay currents over a long period of time, and it has been observed that the current depends on such experimental conditions as the intensity of electric field and temperatures.

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In this study polyethylene has been selected as sample material that represents cross linked material with the most fundamental structure, among high polymers, to find out the generally recognized phenomenon of electric conduction and absorption current. And the characteristics of the temperature change before and after the irradiation of ^{60}Co γ -rays has been described. Changes in electric properties and the decay of conducted current as well as the temperature dependence were also observed.

II. Experimental Methods

1. Specimens

Unirradiated polyethylene as a low density sheet which was (sumikathene G201) prepared through high pressure method was solidified, without additives, by being cooled down at the normal temperature of 130-140°C. Its melting point was recorded as 106°C, and the molecular weight was 40,000. The degree of crystallization analyzed through X-rays was 65 percents, and it formed a film of 0.5-1 mm thick.

Radiation-irradiated polyethylene was irradiated on this film in the open air by the ^{60}Co γ -ray sources (intensity: about 500 ci) to decide the amount of the absorbed dose after the irradiation. Total dose was computed with the aid of existing value of the source intensity measured by the Korea Atomic Energy Research Institute.

2. Experiment

The arrangement of the equipment for measuring the electric conduction is shown in Fig. 1.

The electrode for the measurement of the sample material has two rounded gold leaves of 40mm in diameter, applied on both sides with vaseline³⁾. Silver guard-rings were also attached on both sides so that the errors occurred during the measurement due to damages of the electrode's surface might be counted. If this process comes just before the irradiation, those closely adhered materials will be easily changed in their qualities by the irradiation. Then it will be difficult to distinguish the changes of them from those of the sample material; eventually the repeated use of the same sample would also be impossible.

However, in this experiment, the experimenter inserted guard-rings after forming two electrodes, the main and the guard, as shown in Fig. 2 on the surface of the polyethylene to get a satisfiable result³⁾.

Sometimes when the magnitude of measured current reached less than 10^{-12}A , the Keithley Multirange Electrometer 610B or 610 BR was employed. The highest degree of sensitivity of this electrometer was turned out to be 10^{-14}A while the measured current by it ranged from 10^{-14}A to 10^{-9}A . The degree of precision of measured current also ranged from $\pm 2\%$ at 10^{-9}A to $\pm 4\%$ at 10^{-12}A .

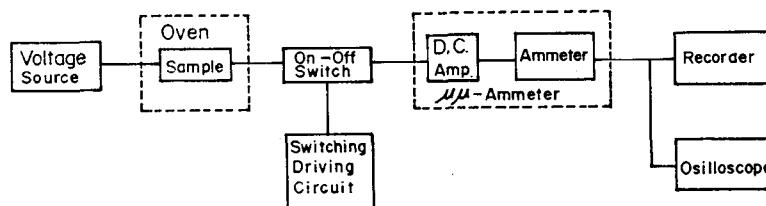


Fig. 1. Block Diagram of Measuring System

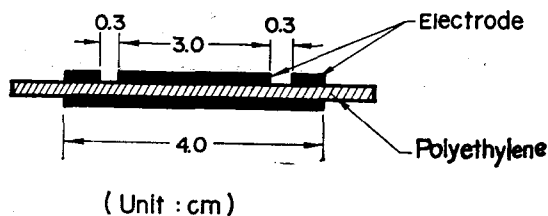


Fig. 2. Electrodes for Measuring Electrical Conduction

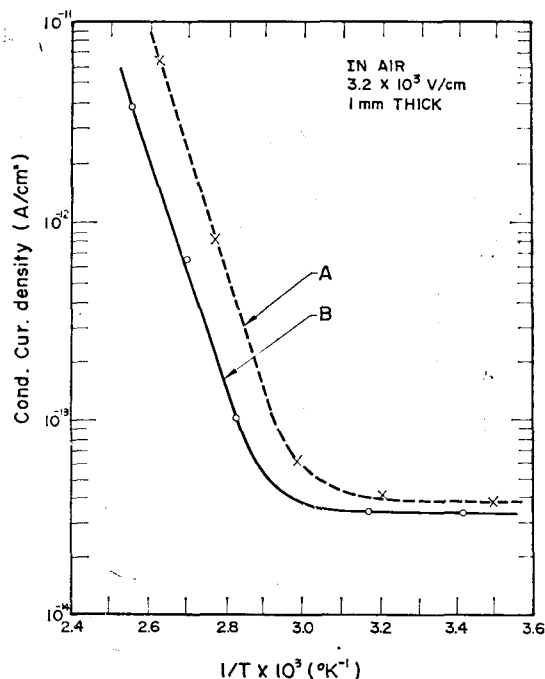


Fig. 3. Effect of Irradiation on Temperature Characteristics of Conduction Current in Polyethylene

For measurement of the temperature of the sample, a thermocouple was used with a direct current VTVM. The thermocouple was attached to the inside of the electrode. At the same time, the lead which protruded from the mass electrode was thrown outside of the vacuum vessel, so that it could be connected to a $\mu\mu$ -electrometer.

III. Result and Discussion

1. Measurement of temperature

Fig. 3 represents the resulting current

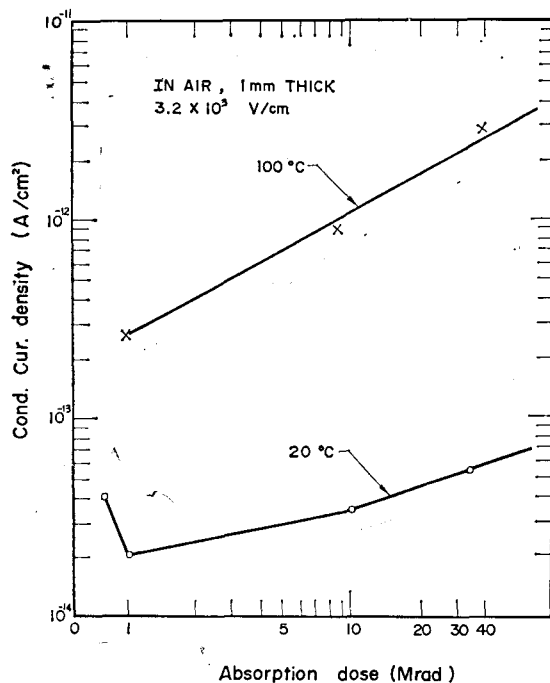


Fig. 4. Dependence of Conduction Current in Polyethylene on Absorption Dose

density after the voltage application through the electric field of 3.2×10^3 V/cm for 15 seconds on the sample material irradiated with 1.39×10^5 rad in the air. In this figure, curve A represents the results obtained with the sample including additives, while curve B gained with no additives. It was found that the sample showed very little temperature dependence at the normal temperature whether it had additives or not. And it developed a new process that had an outward activation energy neared almost 0 eV. Meanwhile, at the high temperatures, activation energy as well as the electric current increased when the sample included additives.

From the result, it seems clear that electric current decreases at the normal temperature and increases at the high temperatures, in the case of radiation-irradiated polyethylene, without any relationship with the presence

of additives.

2. Absorption dose and temperature dependence

After sample materials of 2 Mrad, 12 Mrad and 35 Mrad were individually irradiated, they were put into an electric field for the heat-treatment at 100°C. In the same electric field of $3.2 \times 10^3 \text{ v/cm}$, the absorption dose was measured at the temperature of 20°C and 100°C respectively. The result is shown in Fig. 4.

If the electric current dependence of the absorption dose (R) would be expressed like $J \propto R^n$, the value of n turned out to be about 0.88.

When the temperature was fixed at 20°C, the value of current showed a slow increase.

3. Volume resistivity and temperature dependence

Fig. 5 shows the relationship of volume resistivity versus $1/T$ when the low density polyethylene was irradiated in the air. The volume resistivity of the irradiated sample material has shown a decrease in accordance with the increasing radiation dose of irradiation at the room temperature.

Changes in $\log(\rho)$ versus $1/T$ characteristics were observed:

When the temperature kept below 60°C, the observed characteristic curve exhibits decrease of the value of $\log \rho$ with increasing temperature. The decrease of the curve slowed down before it increase rapidly along with the temperature near the melting point of crystalline region. This phenomenon was closely observed when the absorption dose recorded more than 10^6 rad. This can be interpreted as the collapse⁴⁾ of the crystalline regions when there exists a large dose irradiation. Furthermore, there is a report⁵⁾ that

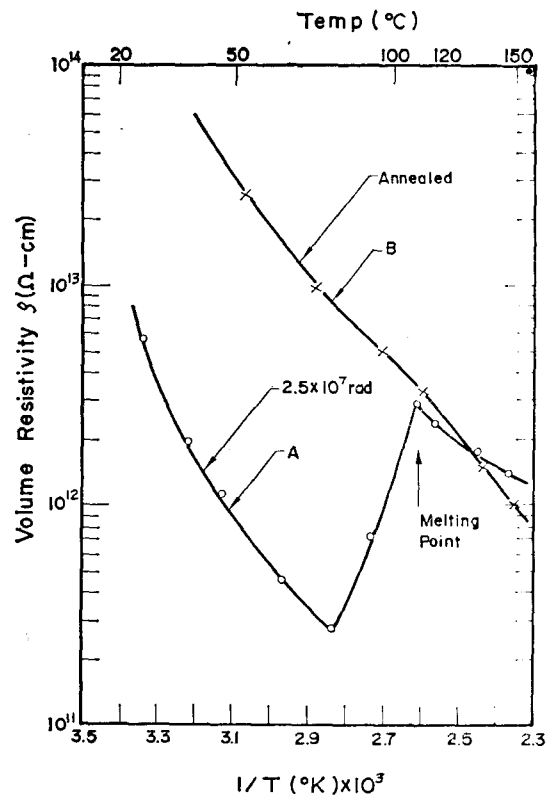


Fig. 5. Temperature Dependence of Volume Resistivity of Gamma Ray Irradiated Low Density Polyethylene

the low density polyethylene begins to melt, against the parts of crystal, at the melting point; while in the lower temperature range, the crystal parts begin to melt.

Compared with these findings, the jumping phenomenon⁶⁾ of (ρ) has a tendency to the changes in the degree of crystallization, and one can conclude that there is a close relationship between the jumping phenomenon and the melting in crystalline regions.

Another different characteristics in $\log(\rho)$ versus $1/T$ relationship was observed when the irradiated sample of polyethylene was heated above melting point. As shown in Fig. 6, there appeared no jumping in this circumstances; the reduced (ρ) by irradiation and the activation energy both developed another phenomenon quite different from the

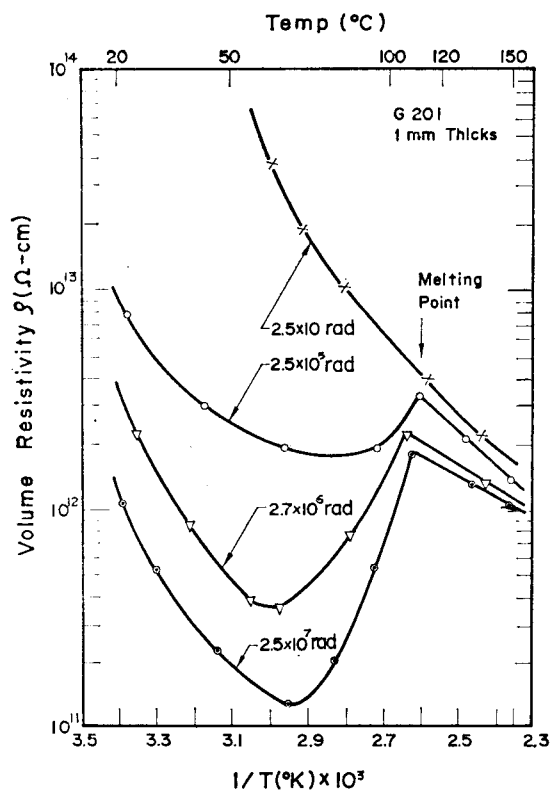


Fig. 6. Effects of Annealing on Temperature Dependence of Volume Resistivity of Gamma Ray Irradiated Low Density Polyethylene with 2.5×10^7 rad

result gained during the initial heating process. And when the irradiated material which was once heated was cooled down, after a suspension period of initial heating, and when it was reheated, the (ρ) versus $1/T$ characteristics recorded a value similar to that gained during the initial heating process. This can be explained as having close relationship with the temperature increase up to the melting point of crystals by the effect of annealing. In the figure 6, curve A represents the results gained during the initial heating process, while curve B during the cooling down process.

4. Measurement of the infrared absorption spectrum

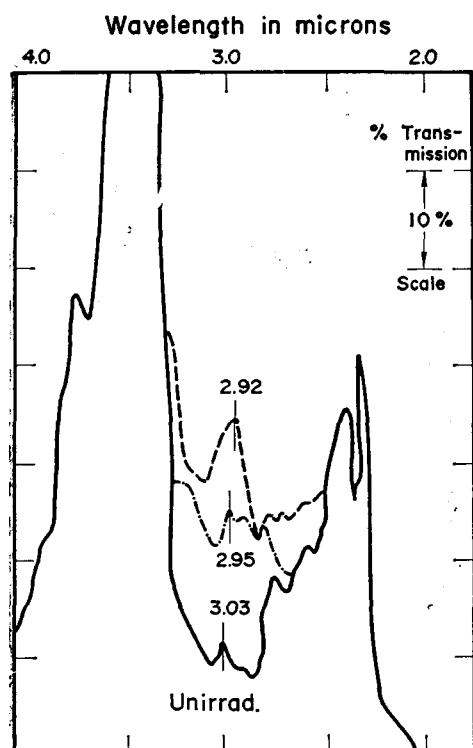
When analyzing the effect of irradiation

on the structure of the 0.08 mm thick unirradiated polyethylene film, as seen through the infrared absorption spectra, carbonyl radicals of 5.8μ were found after the pre-irradiation with γ -ray of 1.39×10^5 rad/hr. This formation of carbonyl radicals was thought to be closely related to the solubility, diffusion⁷⁻⁸⁾ of the oxygen against polyethylene and at the same time to the degree of crystallization of polyethylene itself. As shown in Fig. 7, the act of absorption of OH-radical was observed at around 2.9μ . It was recorded 2.95μ when the irradiation was 3.4×10^7 rad and 2.92μ when 10.48×10^8 rad, showing rapid increase as the absorption dose increased. This increase is believed to be caused by the fact that the sample material was so thin and it was irradiated over long period of time. And the creation of oxidation product from among the molecules of polyethylene also played a part of role.

5. Decay of conduction current and dependence of temperature

As the effect of the orientation polarization caused by the polar groups was very insignificant during the decay process of current in polyethylene, meanwhile another decaying current was considered in relation with the transport phenomenon of the electric charge for polarization.

Recently, there have been many reports made on the electronic states of noncrystalline materials. With the recognition of the importance of the localized states⁹⁾, two possible mechanisms have been proposed to describe the charge transport phenomenon; these are referred to as a band type conduction due to the excitation of unlocalized states and a hopping type conduction due to the phonon assisted tunneling of an electron



Irradiated polyethylene
Fig. 7. Infrared Absorption Spectra of Irradiated Polyethylene

from one localized state to another¹⁰. In the material which shows random state of various structures like polyethylene, the band type conduction is more favored than the hopping type. According to McCubbin¹¹, the intermolecular mobility of holes reached more than $50 \cdot 10^{-3} \text{ cm}^2/\text{v. sec.}$ by the theoretical calculation. It was found, however, in the experiment to be $10^{-3} \text{ cm}^2/\text{v. sec.}$ and this opened up a new possibility of the presence of the localized state.

The current density¹² J for the hopping type conduction was expressed by Pollack and others briefly as follows:

$$J = ne(\langle x_1 \rangle - \langle x_2 \rangle) (1/\tau) \times [f_1(\infty) - f_1(0)] \exp(-t/\tau) \quad (1)$$

In this formula x_1 and x_2 represent coordinates of the carriers toward the electric field

in each state; τ is the single decay constant; n is the density of the charge carrier and f is the occupation probability.

From this formula, it is clear that the change in electric current depends on the single(τ). Various transitions between hopping are expected to be possible and they would be expressed by single(τ). This same formula shows that when $t > \tau$, the contribution of the electric current through the transition related to (τ) would rapidly be cut short. Temperature dependence of the transition probability, when the simple barrier caused by $1/(\tau)$ in Eq. 1 is considered, would be expressed in the following:

$$\begin{aligned} \omega(\text{transition probability}) \\ = \nu \exp(-u/kT) \end{aligned} \quad (2)$$

In which u indicates the height of the potential barrier and ν represents the vibration frequency. The contribution resulted from the relationship existing between τ and u on the electric current is rapidly reduced with the time. Accordingly, if there exist various transitions, their contribution on the current near $t \simeq \tau$ would also be reduced with the time spent.

Characteristics of the electric conduction of the radiation irradiated polyethylene can be summarized as follows:

It created small value of current than the unirradiated polyethylene during the process forming the initial activation energy of 0 eV after the voltage application. This current was increased until it exceeded that from the unirradiated polyethylene with the time lapse. In the radiation irradiated polyethylene, a trap level was introduced for the hopping organs which have small gaps of energy, and the effect of trap played an important role during the transition process¹³.

Transition probability can be counted through the following formula:

$$\omega = \omega n_c \tau_c / (n_c \tau_c + n_i \tau_i) \quad (3)$$

where n_i corresponds to the trap density; $n_c \tau_c$ represents the time spent in trap; $n_i \tau_i$ is the time spent outside of the trap. According to this formula, the current value is continuously being reduced although some contribution can be made from the transitions of great energy gaps. However, a considerable amount of donor seemed to be introduced by the radiation irradiation.

IV. Conclusion

The electrical conduction of the irradiated polyethylene in relation to the temperature changes, and the influence of temperature on the volume resistivity at the melting of crystalline would be summarized as follows:

1) In the case of low density polyethylene, irrespective of the presence of the additives, the electric current is small and nearly constant at temperatures near room temperature and below, while it increases rapidly with temperature at higher temperatures.

2) In case the absorption dose remains constant, the electrical conduction proceeds more actively at high temperatures than it does at lower temperatures. And the relationship between the absorption dose and the electrical conduction can be expressed as $J \propto R^n$.

3) As for the temperature dependence of the volume resistivity, the rapid increase of (ρ) at the melting point of crystal and the effect of annealing seemed to be closely related

to the trap caused by the degradation of crystals by radiation.

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