

실리콘유 접촉을 사용한 LDPE의 전기전도 현상

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Electrical Conduction of LDPE with Silicone-oil Contact

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요 약 : 20~100°C까지의 온도범위 및 75~650 kV/cm의 전기장 범위에서 표면에 실리콘유를 바른 저밀도 폴리에틸렌의 전기전도특성을 조사하였다. 연구결과, 폴리에틸렌의 전도전류는 전기장에 따라 지수적으로 증가하며 온도가 높아질수록 증가함을 알았으며, 폴리에틸렌의 전도특성을 공간 전하제한전도와 터널링 효과에 의한 파울러-노드하임전도로서 설명하였다. 전기전도에 대한 활성화에너지는 90~450 kV/cm 범위에 걸쳐서 0.54~0.44 eV 정도의 값을 가지며 전하이동도는 온도에 따라 10^{-16} ~ 10^{-14} m²/V·s 정도의 값을 가지는 것으로 추정된다. 본 실험결과, 폴리에틸렌의 표면에 있는 실리콘유로 인하여 폴리에틸렌의 전기전도특성이 상당히 변하는 것으로 밝혀졌다. 주요한 변화로는 (1) 전도전류의 크기가 증가하며, (2) 180~300 kV/cm 범위에서 전도전류의 증가폭이 크게 둔화되며, (3) 활성화에너지의 감소 등이다.

Abstract : Electrical conduction characteristics of low density polyethylene with a silicone-oil layer at the surface have been investigated at medium fields ranging from about 75 to 650 kV/cm over the temperature range of 20 to 100°C. The conduction current of polyethylene increases exponentially with the electric field and gets higher at higher temperatures. The observed conduction behavior was explained in terms of the SCLC and Fowler-Nordheim conduction by a tunneling effect. Activation energy ranges from 0.54 to 0.44 eV over the field range of 90-450 kV/cm and the charge mobility was estimated from a Child law to be in the order of 10^{-16} - 10^{-14} m²/V·s. The silicone oil layer modifies the conduction behaviors in polyethylene. Major changes are (1) an increase in conduction currents, (2) a suppression in a rate of change of conduction currents, and (3) a decrease in activation energy.

INTRODUCTION

As the industrial requirements for power transmission or distribution are getting stricter, a higher voltage reliability of insulating materials becomes important and to meet these versatile test methods have been developed. When the test voltage is high, the materials under test are generally immersed in an insulating oil in order to prevent a premature failure resulting from such phenomena as flash-over or corona discharge. Recently, the use of silicone oil has become widely adopted.

In tests involving voltage, the contact between the specimen and electrode becomes important because the nature of contact might be modified due to the oil layer. The effect of a thin oil layer may be neglected when the test voltages are very high. However, when the test voltages are intermediate, for example, in the range of hundreds kV/cm, the thin oil layer may affect the measurement of the insulation characteristics of the test materials. Typical examples which may be influenced by such a thin oil layer would be the conduction characteristics and charge injection. Of these, the conduction characteristic is one of the most fundamental phenomena in the electrical insulation, because it governs the conduction of charges (i.e., transport of charges) in such materials as semiconductors, ceramic insulators as well as polymeric insulators.

The current flow in polyethylene has been studied for years in order to understand the charge transport phenomena. As a result, such conduction mechanisms as ionic, ohmic, space charge limited conduction (hereafter SCLC), Schottky, or Poole-Frenkel models have been proposed for explaining the conduction characteristics in polyethylene.¹⁻⁵ Now, it is generally accepted that the ohmic conduction is dominant at low fields and the SCLC at high fields, the threshold field being in the range of tens kV/cm, and that the ionic conduction becomes predominant when ionic impurities exist.⁶⁻⁸

Most of these studies were done using the vacuum evaporated metal electrodes in which a

good contact might be assumed. However, results obtained with this type of electrode cannot be directly applied to the situation where the oil-immersed test system is in operation.

In this study, therefore, the conduction characteristics of silicone-oil pasted on low density polyethylene have been evaluated at the temperature range of 20 to 100°C and the effect of silicone oil on the conduction behavior has been discussed.

EXPERIMENTAL

As-received commercial LDPE without any additives provided by Hanyang Petrochemical Co., Korea, was used throughout the study. This polyethylene is being used as an insulation of medium voltage power cables. Its density and melt index are 0.920 g/cc and 0.20 g/10 min., respectively.⁹ Details on other properties are not known. Typically 30-40 μm thick films were compression molded by Carver Laboratory Press at 180°C.

Figure 1 shows a wiring diagram for measuring the charging current. It consists of power supply (Keithley 247), electrometer (Keithley 617), and electrode system in which the measuring electrode is connected to the electrometer and the counter electrode to the power supply. Silicone-oil contact was obtained simply by pasting some silicone oil on both surfaces of polyethylene film and spring-tightening between two Al electrodes. In this case, the thickness of silicone-oil layer is not known. The area of the measuring electrode was 6.06 cm². The temperature control from 20~100°C was

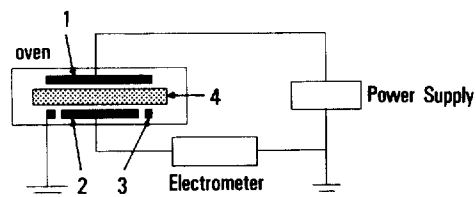


Fig. 1. Wiring diagram for measuring the charging current : (1) counter electrode, (2) measuring electrode, (3) guard ring, (4) test film.

achieved by placing the test cell in an air-convection oven. The measurement was done at 20°C first then the test temperature was ramped up to the next test temperature without changing the test film.

RESULTS AND DISCUSSION

Careful attention has to be paid in determining the steady state current as a function of charging time, because the transient current changes for a long period of time after the application of dc field. Previous reports^{5,10} have revealed that steady state currents taken at different times change the magnitude only in an *i*-*V* plot. Also, only a minor change in magnitude was reported when the steady state currents were taken after 40 min. In this study, therefore, all steady state currents were taken at 40 min after the application of the dc field.

Figure 2 shows the *i*-*V* characteristics of LDPE film at the temperatures ranging from 20 to 100°C. As expected, the steady state current increases, typically from 10⁻¹⁰ to 10⁻⁸ A for 70°C, as the voltage increases from 250 to about 2000 V corresponding to 75 to about 600 kV/cm. Also, higher steady state currents were observed at higher temperatures.

In this figure four linear regions showing different rates of change of conduction current as a function of voltage are observed. These were identified as Region I, II, III, and IV in the order of increasing voltage. The temperature seems to play an important role in developing those regions. At low temperatures such as 20 and 50°C, it is difficult to distinguish each region, but becomes more pronounced as the temperature increases. Above 70°C, the four regions are clearly distinguishable. Between Region I and III, Region II where a rate of change of conduction currents is considerably suppressed was observed in the present study. It seems that Region II exists at all temperatures, though barely distinguishable at low temperatures.

One of the classical treatments of *i*-*V* plots is to predict the conduction mechanisms from the

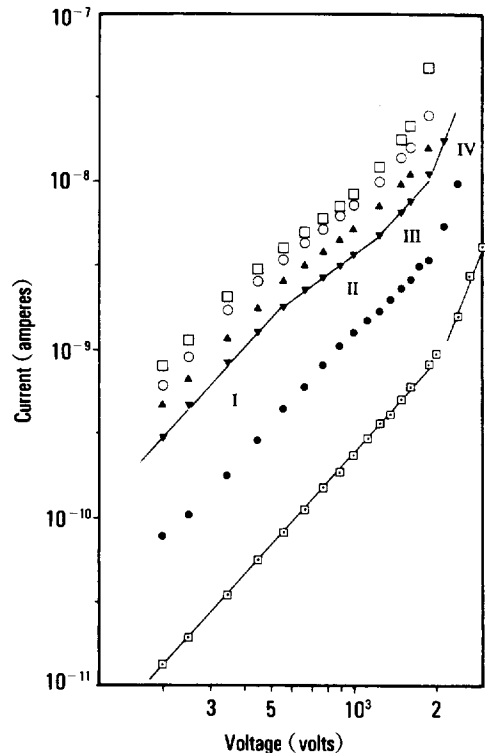


Fig. 2. *i*-*V* characteristics of LDPE film : 20°C(□), 50°C(●), 70°C(▼), 80°C(▲), 90°C(○), 100°C(□).

slope.¹¹ A linearity in log *i* vs. log *V* curves represents the ohmic or SCLC mechanisms and a nonlinearity comes from the Schottky, Poole-Frenkel, or Fowler-Nordheim conduction mechanisms. When the linear relationship holds true, the steady state current can be expressed as $i \propto V^n$. Generally speaking, $n=1$ represents the ohmic conduction and $n=2$ the SCLC. Besides, such factor as a thickness dependence of conduction currents has to be taken into account to get a better assignment of the conduction mechanism.

The average value of power index, *n*, was estimated by a least square fit to be 2.04 for Region I, 1.42 for Region II, 2.13 for Region III and 5.54 for Region IV. Immediately, one can notice that no ohmic conduction region was observed in the present study, possibly due to the range of electric field employed which is somewhat higher than those in other reports.^{5,7} Literature information indicates

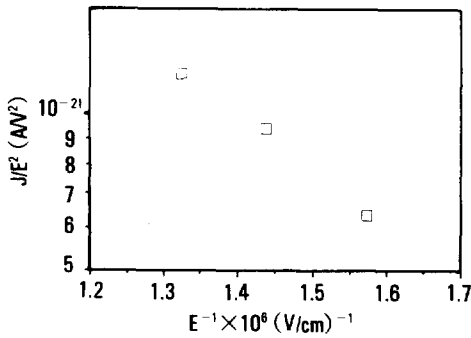


Fig. 3. Fowler-nordheim plot for region IV : data obtained at 20°C.

that the transition from the ohmic to the SCLC occurs roughly at 8~10 kV/cm.^{5,10,11}

The conduction mechanism for Region IV is relatively simple. Region IV showing a strong dependence of conduction current on the applied field has an average power index of 5.54. Also, non-destructive current pulses known as a precursor for the dielectric breakdown¹² were observed in this region. A Fowler-Nordheim plot, $\log(J/E^2)$ vs. $1/E$, for Region IV is in Figure 3. For this purpose, the data at 20°C was used simply because the 20°C result has more data points than the 70°C one. A linearity in a plot of $\log(J/E^2)$ vs. $1/E$ is observed, indicating that Region IV can be assigned as a Fowler-Nordheim conduction region caused by a tunneling effect. At high electric fields the width of energy barrier may get narrowed sufficiently by the assistance of electric field such that electrons are injected from the electrode into dielectric by a tunneling effect.^{13,17}

The power index for Region I and III is about 2.0 and that for Region II is 1.43. From the values of power index, it seems that the conduction mechanism for Region I and III is the SCLC and that the conduction mechanism for Region II is apparently different from that of Region I and III. However, a thickness dependence of conduction currents shown in Figure 4 suggests that the conduction mechanism for Region II may be the SCLC. In the figure, the slope of -3 for Region I, II and III is observed, which indicates that a Child law works for

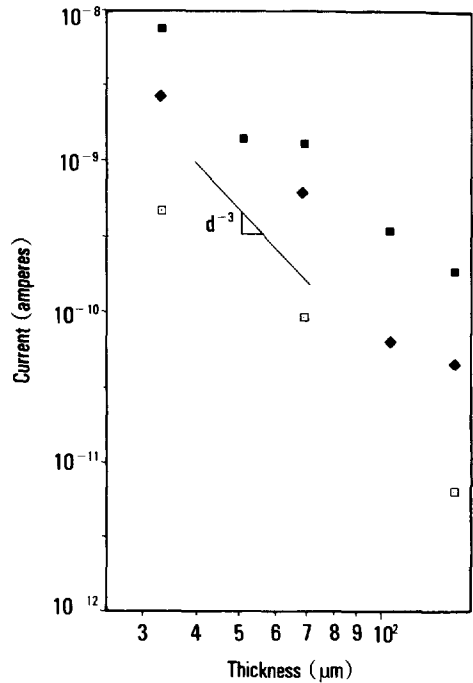


Fig. 4. Thickness dependence of conduction currents: 300 V(□), 900 V(◆), 1500 V(■).

these regions. A Child law is a typical theoretical expression for the SCLC mechanism. The reason for the presence of Region II, i.e., a considerable suppression in a rate of change of conduction currents vs. voltage, is not clear at this point. One possibility is that the nature of contact might be modified due to the silicone-oil layer. This is to be discussed later.

The activation energy for the conduction was obtained using the following Arrhenius-type equation : $\sigma = \sigma_0 \exp(-\Delta E/kT)$, where σ_0 represents a pre-exponential factor, ΔE the activation energy, k a Boltzmann constant and T an absolute temperature. From this equation, the activation energy for the electrical conduction can be estimated from the slope of a $\log \sigma$ vs. $1/T$ plot. Figure 5 shows the relationship between the conductivity and the reciprocal absolute temperature. Apparently, a linear relationship between $\log \sigma$ and $1/T$ was not observed, deviating from linearity at high temperatures. This nonlinearity may originate from the

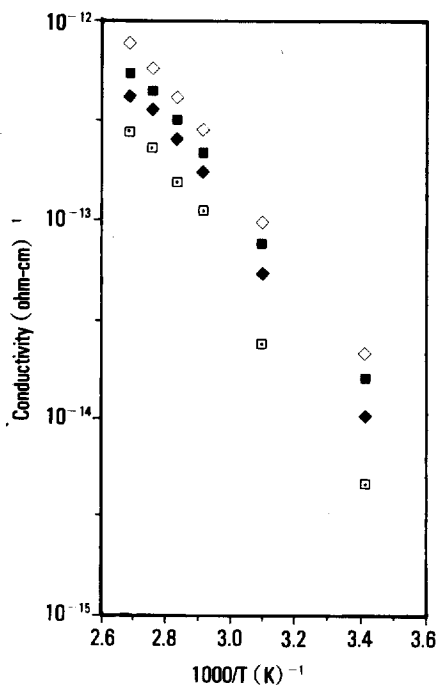


Fig. 5. dc conductivity as a function of the reciprocal absolute temperature : 120 kV/cm (\square), 240 kV/cm (\blacklozenge), 364 kV/cm (\blacksquare), 450 kV/cm (\diamond).

morphological change with the temperature, as pointed out by Hugues St-Onge.¹⁰ As the temperature reaches the point where the chain motion is enhanced, the motion of charges becomes active so that the conduction becomes easier than at lower temperatures, resulting in a decrease in a slope in a $\log \sigma$ vs. $1/T$ plot. Also, the voltage dependence of activation energies shown in Figure 6 exhibits a continuous decrease from 0.54 to 0.44 eV as the electric field increases from 90 to 450 kV/cm. A similar observation has been reported elsewhere.¹⁰ However, the magnitude of activation energies observed in the present study are somewhat lower than those reported by others. The reported ones are 0.60~1.10 eV.^{1,3~5,7}

The effective charge mobility can be calculated from the following Child equation : $J = (9 \epsilon \epsilon_0 \mu_{\text{eff}} V^2 / 8 d^3)$, where J is the current density, ϵ the relative permittivity (2.5 for PE), ϵ_0 the permittivity of free space, μ_{eff} effective charge mobility, V the

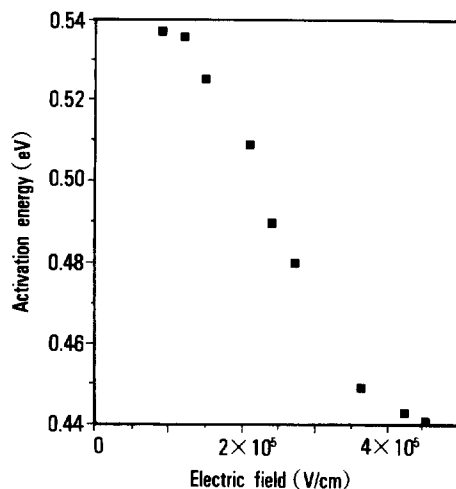


Fig. 6. The field dependence of activation energies :

applied voltage, and d the film thickness. Also, the temperature dependence of the effective charge mobility is of the form, $\mu_{\text{eff}} = \mu_0 \exp(-\Delta E/kT)$, where μ_0 is a pre-exponential factor, ΔE an activation energy, k Boltzmann constant and T the absolute temperature. The temperature dependence of effective charge mobility was shown in Figure 7, where the effective charge mobilities calculated at various temperatures were plotted against the $1/T$. As shown in Figure 7, the linear relationship was not observed for the whole temperature range tested. At high temperatures, a rate of change of the effective mobility decreases as the temperature increases. This was discussed in the above with Figure 5. It has been found that the mobility of silicone-oil pasted LDPE estimated from the data of low temperatures ranges from 10^{-16} ~ 10^{-14} $\text{m}^2/\text{V} \cdot \text{s}$ depending on the temperature, which agrees well with the values obtained by others.^{7,8,10} The activation energy calculated from the slope was 0.50 eV, which agrees again well with the value from Figure 5.

Experimental results obtained in the present study agree, in most parts, with those that have already been reported. The conduction current increases exponentially with the electric field and increases as the test temperature increases. Also,

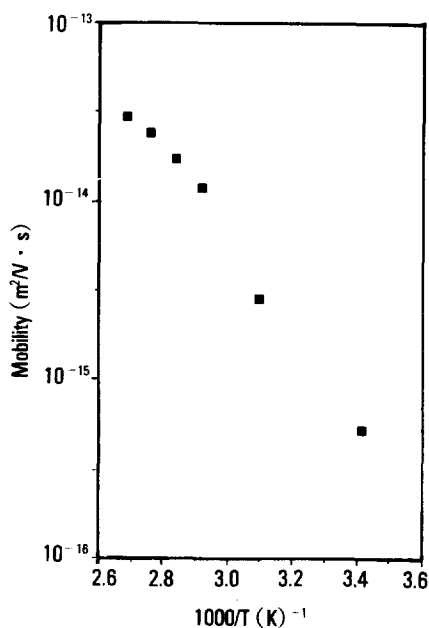


Fig. 7. The temperature dependence of effective charge mobility :

the SCLC and Fowler-Nordheim conduction mechanisms are observed in the present study. Others have observed this using other types of electrodes. Based upon the present observations, however, it seems that the silicone oil contact changes the conduction behavior in polyethylene. The observations which are different from the reported ones are as follows :

- (1) The magnitude of conduction currents is high compared to others.
- (2) A considerable suppression in a rate of change of conduction current vs. voltage was observed.
- (3) The range of activation energies is lower than those reported previously.

The magnitude of steady state currents measured in the present study is higher by about 3 orders compared to the reported one. As far as the activation energies are concerned, it seems that different electrodes yield different activation energies, as pointed out by W. G. Lawson.³ For example, vacuum-evaporated Al electrode produced an activation energy of 0.85 eV, while the graphite

electrode produced an activation energy of 1.05 eV. A suppression in a rate of change of conduction current vs. voltage has been reported in PVDF.¹⁴ Sometimes, a negative resistance characteristic has been reported in polyethylene and polypropylene.^{15~17} However, the suppression observed in the present study and in PVDF seems not to be the same type of negative resistance in the sense that the former shows a positive slope whereas the latter shows a negative slope in an *i*-*V* plot. Some claim without experimental evidence that such suppression is due to the morphological change brought about by the electric field.^{14,15} However, the present results suggest that such suppression may not be a matter of the morphological change but a matter of contact. In other words, the nature of contact at the LDPE-electrode has been modified, one obvious possibility being the formation of triple-layered capacitor, i.e., silicone oil-LDPE-silicone oil between two electrodes.

In order to make this argument clear, the conduction behavior of the same LDPE was evaluated using a sputtered Al electrode. The result at 70°C is shown in Figure 8 where the result is compared with the electrode attached by a thin film of silicone oil at the same temperature. The conduction current of the sputtered Al electrode ranges from 10⁻¹² to 10⁻¹⁰ A at comparable electric fields, about 2 order lower at comparable electric fields than that of silicone oil contact. Also, the slopes in a log *i* vs. log *E* plot are 1 at low fields, 2 at medium fields, and about 4 at higher fields. A more pronounced difference is that no marked suppression in a rate of change of conduction current vs. voltage was found when a sputtered Al electrode is used as a contact. The conduction behavior of LDPE with the sputtered Al electrode at other temperatures is being currently evaluated along with other types of electrode. The results observed so far confirm that the above mentioned differences may originate from the contact. That is, silicone oil modifies the nature of contact so that the resultant conduction behavior is altered. At this point, however, what types of modification have occurred

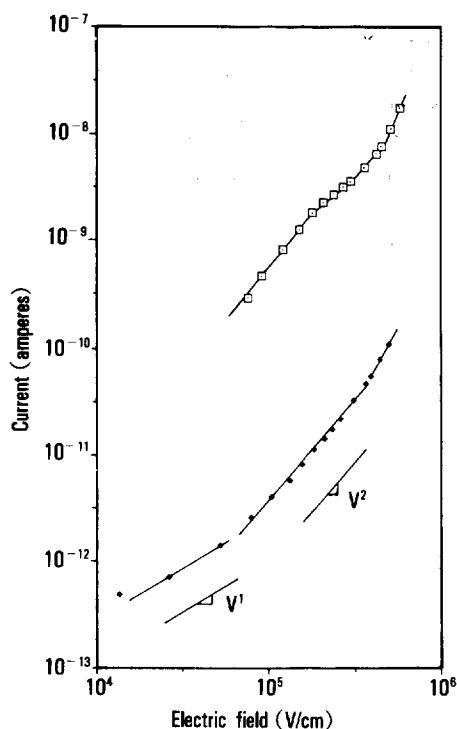


Fig. 8. Comparison of i - E characteristics of silicone oil contact and sputtered Al electrode at 70°C : silicone oil contact(\square), sputtered Al electrode(\blacklozenge).

is not clear.

Nonetheless, the conduction mechanism for Region II seems not to be changed (that is, the SCLC) because a thickness dependence of conduction current ($\log i$ vs. $\log d$) has yielded the slope of -3 (Figure 3) and because a smooth change in an ΔE vs. E plot has been obtained (Figure 6).

In conclusion, the silicone oil changes the conduction behavior of low density polyethylene, the major changes being (1) an increase in conduction currents, (2) a suppression in a rate of change of conduction currents, and (3) a decrease in activation energy. Exact reasons for such changes are not known.

CONCLUSIONS

The study of the electrical conduction characteristics of the silicone-oil pasted LDPE has revealed

the following major results:

(1) The conduction current of the oil-pasted low density polyethylene increases exponentially with the applied voltage and gets higher as the temperature increases.

(2) Four regions in an i - V plot have been observed, assigned as Region I, II, III and IV in the order of increasing voltage. The SCLC may be predominant in Region I, II and III, and a Fowler-Nordheim conduction by a tunneling effect may be responsible for Region IV.

(3) In Region II at $180\sim 300$ kV/cm, a rate of change of conduction current vs. voltage was suppressed. This suppression may originate from the silicone oil used as a contact.

(4) Activation energy decreases from 0.54 eV at 90 kV/cm to 0.44 eV at 450 kV/cm and the effective charge mobility changes from 10^{-16} to 10^{-14} $\text{m}^2/\text{V}\cdot\text{s}$ at the temperature range of 20°C to 100°C .

These results indicate that the conduction characteristics of polyethylene can be modified due to the silicone oil layer used as a contact. Major changes are (1) an increase in conduction currents, (2) a suppression in a rate of change of conduction currents vs. voltage, and (3) a decrease in an activation energy. Currently works are in progress to explain such changes due to the silicone-oil layer.

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