

# Effects of Constituents of XLPE on the Formation of Space Charge

Kwang S. Suh, Sun J. Hwang,  
Jin S. Noh

Department of Materials Science, Korea University,  
Seoul, Korea

and Tatsuo Takada

Department of Electrical and Electronics Engineering,  
Musashi Institute of Technology, Tokyo, Japan

## ABSTRACT

The effects of such constituents as the crosslinked part, non-crosslinked LDPE part, antioxidant, and residual byproducts on the formation of space charge in XLPE have been investigated. It has been found that homocharge is developed in the pure crosslinked part of XLPE. The non-crosslinked LDPE part encourages the formation of heterocharge, although its influence is not strong. Residual byproducts generated during the crosslinking reaction encourage the formation of heterocharge, whereas antioxidant was found to prohibit the formation of heterocharge. Of these, residual byproducts have been found to impose the most pronounced influence on the formation of heterocharge in XLPE, so that only heterocharge is found in an as-pressed XLPE with semiconductive electrodes.

## 1. INTRODUCTION

GR<sup>EAT</sup> attention has been paid to research on the charge-related properties of XLPE which is being utilized widely for the insulation of power cables. Of the factors influencing the electrical properties of XLPE, the effects of such low molecular weight molecules as residual byproducts and additives are relatively well characterized. For example, it has been reported that electrical conduction characteristics and the ac breakdown strength of XLPE are influenced strongly by the presence of residual byproducts [1-3] and that the thermally stimulated current (TSC) of XLPE with acetophenone is higher than without acetophenone [4]. The antioxidant affects electrical properties such as treeing, TSC,

and space charge in the polyethylene [5-8].

Despite many reports, the charge accumulation characteristics of XLPE still seem to be ambiguous. For example, electron injection resulting in a homocharge accumulation is known to be the major mechanism for the formation of space charge, whereas the measured spatial charge profile shows heterocharge in XLPE as well as in LDPE [6,9-10]. This discrepancy may be related to the constituents of XLPE, which may be considered to be composed of four parts: a crosslinked part, a non-crosslinked part, additives and residual byproducts. The crosslinked part is not solvent extractable, having a three dimensional network structure formed by the curing reaction,

while the non-crosslinked part is essentially LDPE. The most widely used additive in XLPE is the antioxidant. In addition, there exist such residual byproducts as acetophenone, cumyl alcohol, and  $\alpha$ -methylstyrene formed by the thermal decomposition of peroxides [11]. Since all these constituents can contribute to the formation of space charge in XLPE, we have investigated the contribution of each constituent to get a better insight into the charge formation characteristics.

## 2. EXPERIMENTAL

### 2.1. SPECIMENS AND TESTING

XLPE slabs, 700 to 800  $\mu\text{m}$  thick and 150 to 200  $\mu\text{m}$  thick semiconductive films were crosslinked under pressure at 180°C for 20 min. The XLPE used in this study is composed of LDPE (density: 0.920 g/cm<sup>3</sup>, melt index: 2.0 g/10 min), antioxidant (Santanox<sup>TM</sup> R, 0.4%), and peroxide. The semiconductive material is composed of ethylene vinyl acetate copolymer (EVA), conductive carbon black, and additives such as wax and antioxidant. It has been demonstrated earlier that the composition of the semiconductive material influences the formation of space charge in polyethylene [12]. Therefore, the same type of semiconductive material was used for the electrodes throughout the present study. The semiconductive electrodes were attached to the surface of the specimen using a hot iron for 1 min.

Test specimens were obtained by the following procedures: Residual byproducts were removed by evacuating an as-pressed XLPE at 80°C for 100 h [10,13], which was considered to contain the crosslinked part, the non-crosslinked LDPE part, and the additives. Vacuum degassed XLPE was then subjected to a chloroform extraction under ambient conditions for 48 h to get rid of the additives. This specimen was considered to contain only the crosslinked and the LDPE parts. Finally, chloroform extracted XLPE was immersed in a boiling xylene for 48 h to remove the non-crosslinked part. The degree of crosslinking was measured to be 86%. This specimen was considered to have the crosslinked part only. Extracted specimens were dried in a vacuum at 60°C for 50 h before testing. The designations used for the test specimens are listed in Table 1. In Table 1, 'fresh' stands for the condition where the as-pressed XLPE or semiconductive electrodes were tested within  $\sim 2$  h after curing.

Up to 22 kV dc was applied to the specimen in a step-wise manner. In each step the voltage was applied for 30 min and a spatial charge profile was collected. Then the voltage was turned off and immediately another spatial charge profile was collected. After all these processes had been done, the voltage was ramped up to the next test voltage. The final test voltage was 21.6 kV which corresponds to an electric field of  $\sim 300$  kV/cm.

Table 1.

Designation of test specimens. vac.deg. = vacuum degassed, 100 h, 80°C. BP = boiling point, RT = room temperature.

Specimen code	XLPE	Semicon electrode
XFSF	fresh	fresh
XFSV	fresh	vac.deg.
XVSV	vac.deg.	vac.deg.
XLCh	extr. 48 h, RT	vac.deg.
XLXy	extr. 48 h, BP	vac.deg.

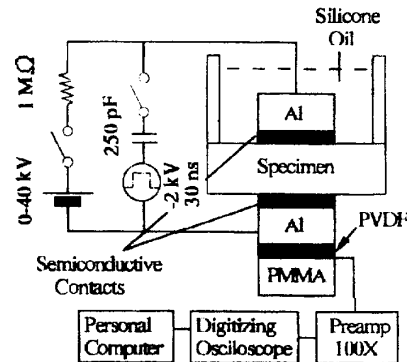


Figure 1.

Schematic diagram of the instrument used to measure the spatial charge profile.

### 2.2. INSTRUMENTATION

An instrument was built to measure the spatial charge profiles. The schematic diagram is given in Figure 1. It consists of a pulse generator to produce electric pulses of the desired pulse widths and amplitudes, a power supply to apply dc stresses for charging the specimen, a test cell which holds the electrodes and the specimen, a detector made of piezoelectric film, and a wide-band digitizing oscilloscope (1 GHz, Hewlett Packard Model 54100 A). A general purpose interface board (GPIB) was used for communication between the instrument and a personal computer.

An electric pulse generator was fabricated to produce stable electric pulses with output amplitudes to  $-4$  kV and a pulse width changeable from 10 to 90 ns. A pulse width of 30 ns and a pulse amplitude of  $-2$  kV were typically used in this study. With this system, an ideal resolution is 60  $\mu\text{m}$ , assuming the sound velocity in XLPE to be 2000 m/s. However, the actual resolution calculated from the measured peak was 98  $\mu\text{m}$ .

The upper electrode was designed to apply simultaneous electric pulses and dc stresses when needed. It is a combination in parallel of a 20 k $\Omega$  resistor and a

250 pF capacitor. A piezoelectric transducer was fabricated to convert the mechanical (electroacoustic) pulse signal generated by the charges inside the specimen into an electric signal. Basically it is a combination in series of a metal electrode, a thin piezoelectric sensor, and a polymer block. A 28  $\mu\text{m}$  thick PVDF film was used as the piezoelectric sensor because of its excellent wide band characteristic in the frequency domain. A polymer block was used as a backing plate to delay reflected signals so as not to interfere with the first signal coming out. Details of the principles and instrumentation have been described elsewhere [14, 15].

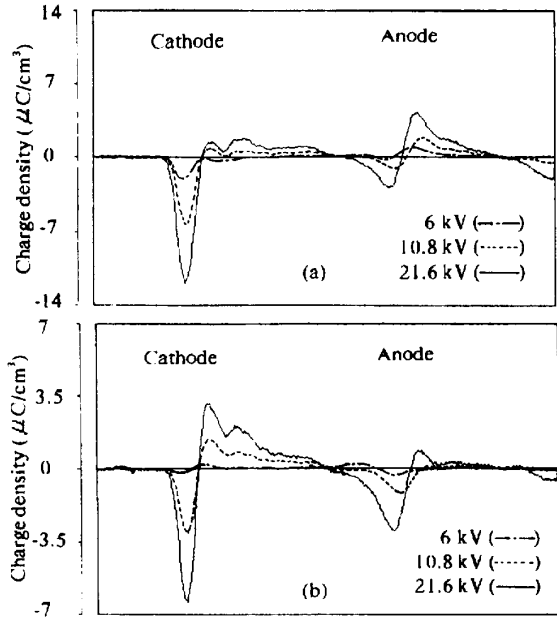


Figure 2.

Spatial charge profiles of XFSF; (a) during voltage application, (b) after voltage removal.

### 3. EXPERIMENTAL RESULTS

#### 3.1. TYPICAL SPATIAL CHARGE PROFILES OF XLPE

Typical spatial charge profiles obtained with a XFSF sample are shown in Figure 2, where the charge profiles collected while dc voltage is being applied as well as after dc voltage is turned off. When the voltage is being applied, as shown in Figure 2(a), XFSF exhibits the formation of heterocharge, i.e., positive charge near the cathode and negative charge near the anode. Heterocharge is also found after the voltage is turned off (Figure 2(b)), the magnitude being larger compared with the size during the voltage application. This change was found predominantly at the cathode side.

It seems that, during voltage application, homocharge injection and heterocharge formation may occur at the same time. The type of charge we see in our spatial charge profiles may be governed by the process which is dominant at the particular stage of measurement. Therefore, small positive peaks are seen during the voltage application because charge injection is active. However, when the voltage is turned off, homocharge injection will not occur so that the heterocharge peak becomes large.

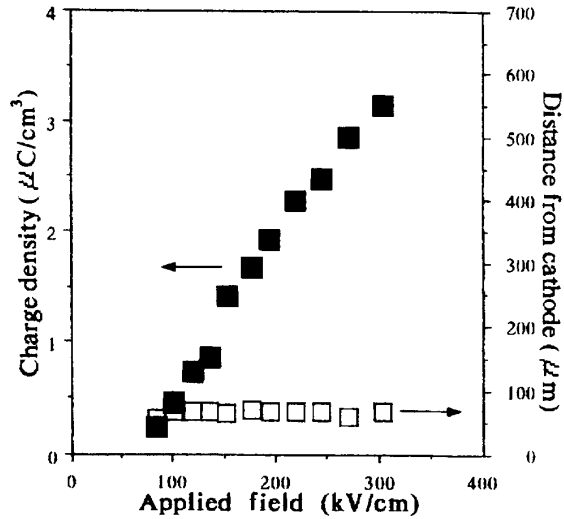


Figure 3.

The peak maxima and peak position of XFSF as a function of applied field.

Peak maxima and peak position as a function of applied field are shown in Figure 3. The peak position remains relatively unchanged and the peak maxima increase with the applied field. This feature is common to all specimens tested in the study.

#### 3.2. THE EFFECT OF VACUUM DEGASSING

The effects of vacuum degassing on the charge formation characteristics of XLPE are demonstrated in Figure 4, where spatial charge profiles of XFSF, XFSV, and XVSV are compared. XFSF shows heterocharge near both electrodes. When the semiconductive electrode is vacuum degassed (XFSV), the magnitude of the heterocharge peak decreases with the shape of the charge profiles remaining unchanged. On the other hand, when both materials are vacuum degassed (XVSV), homocharge was found near both electrodes and no heterocharge peaks are seen.

During the crosslinking reaction, residual byproducts such as acetophenone, cumyl alcohol, and  $\alpha$ -methylstyrene are generated by the thermal decomposition of peroxides [11]. These byproducts are known to be one of

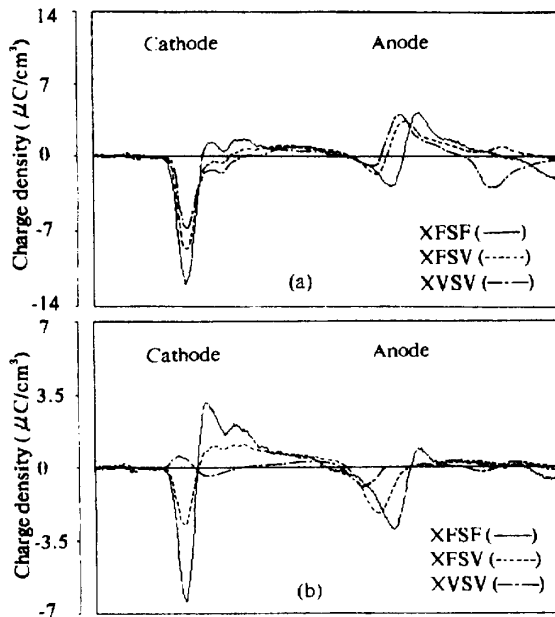


Figure 4.

Spatial charge profiles of XFSF, XFSV and XVSF at 21.6 kV; (a) during voltage application, (b) after voltage removal.

the major sources for the accumulation of heterocharge under high dc stresses [10]. Vacuum degassing removes most byproducts and thus the amount of heterocharge decreases. When the concentration of byproducts is high (XFSF), the heterocharge is dominant over homocharge injection. When most byproducts are removed (XVSF), the reverse is true.

### 3.3. CHLOROFORM EXTRACTED XLPE

Figure 5 shows the spatial charge profile of chloroform extracted XLPE during charging and after discharging. Chloroform extraction was done to see the effect of additives, e.g. the antioxidant.

Peaks corresponding to the injected charge at each electrode were observed when the voltage was being applied (Figure 5(a)). Negative charge penetrates into almost half of the specimen from the cathode and no complicated charge profiles were observed in the center region. After discharge, as shown in Figure 5(b), only a small amount of charge remains. For this, compare the y axis scale of this Figure with those of Figure 2(b) for XFSF and Figure 4(b) for XVSF. Quite interestingly, positive charge peaks were found at low fields whereas negative charge peaks were found at high fields. This feature occurred only at the cathode side.

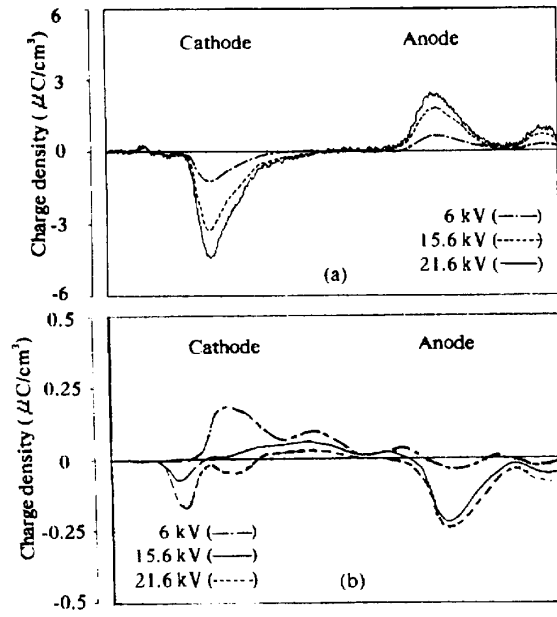


Figure 5.

Spatial charge profiles of chloroform-extracted XLPE (XLCh); (a) during voltage application, (b) after voltage removal.

### 3.4. BOILING XYLENE EXTRACTED XLPE

Spatial charge profiles of a boiling xylene extracted XLPE are shown in Figure 6, where those during charging are in Figure 6(a) and those after discharge are in Figure 6(b). A boiling xylene extraction was made to see the charge formation in the crosslinked part of XLPE.

During the charging step, the shape of charge profiles of a boiling xylene extracted XLPE is very similar to that of a chloroform extracted XLPE. That is, negative charge is found over half of specimen and no complicated charge profile is found in the bulk region. The magnitude of the injected charge peak is smaller than that of chloroform extracted XLPE. After the voltage is turned off, as shown in Figure 6(b), only a small negative charge peak was found at high fields near the cathode, the magnitude of which is comparable to that of chloroform extracted XLPE. Contrary to the case of chloroform extracted XLPE, only negative charge is observed at all fields tested.

## 4. DISCUSSION AND SUMMARY

THE present results have been summarized in Table 2. The contribution of each component to the formation of space charge in XLPE can be deduced from a comparison of the treatment methods and the experimental results. For example, the chloroform-extracted

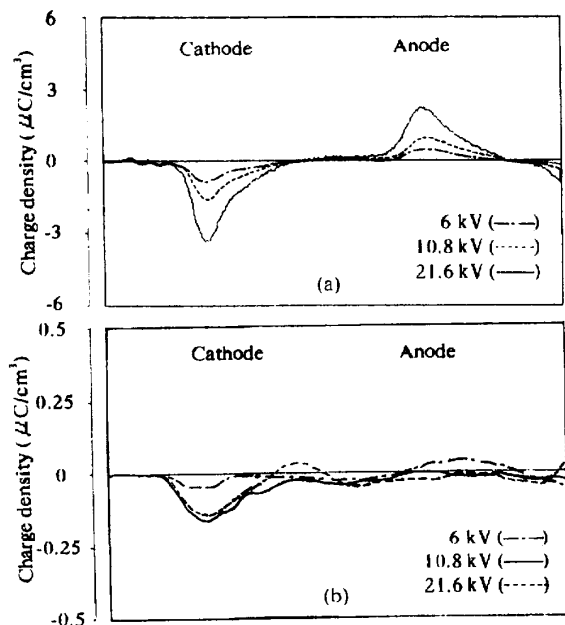


Figure 6.

Spatial charge profiles of xylene-extracted XLPE (XLXy); (a) during voltage application, (b) after voltage removal.

XLPE contains the pure crosslinked part and the non-crosslinked LDPE, whereas the xylene-extracted XLPE contains the pure crosslinked part only. The difference of the results between these samples is the effect of the non-crosslinked LDPE part. The xylene-extracted XLPE shows homocharge and the chloroform-extracted XLPE shows heterocharge at low fields and homocharge at high fields. Therefore, it can be concluded that the non-crosslinked LDPE part of XLPE encourages the formation of heterocharge. However, its effect may not be strong because homocharge is developed eventually at high fields.

Table 2.

Summary of test results. A = antioxidant additive, B = residual byproducts, C = crosslinked part, L = non-crosslinked LDPE part.

Specimen	Component	Results
XFSF	C, L, A, B	hetero
XFSV	C, L, A, B	hetero
XVSV	C, L, A	homo
XLCh	C, L	hetero→homo
XLXy	C	homo

A similar analysis was made to deduce the contribution of each component of XLPE to the formation of space charge, which can be summarized as follows:

1. the non-crosslinked LDPE encourages the formation of heterocharge,
2. the additive (antioxidant: Santanox R) prohibits the formation of heterocharge, and
3. the residual byproducts encourage the formation of heterocharge.

Of these, residual byproducts impose the most pronounced influence on the formation of space charge, so that only heterocharge is seen in an as-pressed XLPE with semiconductive electrodes.

We have shown that the residual byproducts produced by the thermal decomposition of peroxide encourage the formation of heterocharge [10, 13]. The reason might be that the byproducts are low molecular weight molecules so that they are charged easily and may migrate to the counter electrode side under dc stress. The amount of heterocharge accumulated in XLPE will increase with the concentration of residual byproducts.

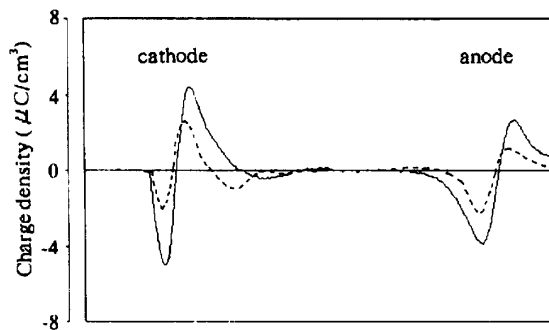


Figure 7.

Spatial charge profiles of XLPE without antioxidants (—) and with antioxidants (---) at 40 kV. Antioxidant: Santanox R, 0.5 pphr.

The effect of the antioxidant used in this work has been studied further. The results are shown in Figure 7. The magnitude of heterocharge near the cathode is considerably reduced by adding 0.5% of antioxidant (Santanox R), while the overall pattern of the charge distribution remains unchanged. The role of antioxidant in the formation of space charge in polyethylene has been reported in the literature [6-8]. One of the results given by Chapeau *et al.* [6] showed a decrease of charge when 0.06% of the primary antioxidant (diphenyl paraphenylene diamine; DPPD) was added to LDPE. Kon *et al.* [7] observed the formation of heterocharge at electric fields below 1.2 MV/cm using a LIPP technique. Suh *et al.* [8] reported that primary antioxidants reduce the heterocharge while secondary antioxidant enhance it. It was also reported that the antioxidant used in that study reduced the heterocharge when its concentration went up to 0.5%. Our present observations are consistent with these earlier results.

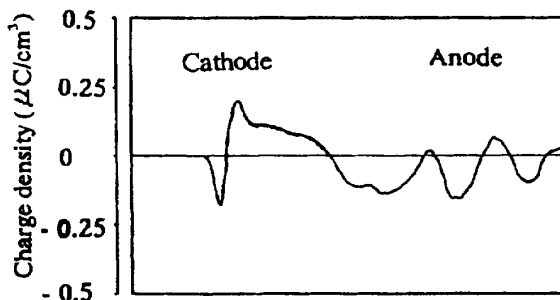


Figure 8.

Charge distribution of pure LDPE at 20 kV.

The spatial charge profile of LDPE used in this study is shown in Figure 8. This LDPE sample was compression molded at 120°C for 10 min and the data was collected at 20 kV. As shown in Figure 8, heterocharge is accumulated near both electrodes. These results confirm the present observation that the non-crosslinked LDPE encourages the formation of heterocharge. It seems, however, that the molecular structure of the LDPE component in XLPE is somewhat different from that in the pure LDPE. The non-crosslinked LDPE part in XLPE is confined to the crosslinked sites, so that the polymer chains are more or less rigid. However, the polymer chains in the pure LDPE are more flexible. The flexibility of the polymer chain may affect the formation of space charge, though this has not been investigated yet, and more work is needed.

The most striking feature of the present study is that heterocharge is observed in an as-pressed XLPE whereas homocharge is observed in a xylene-extracted XLPE. In order to support this observation, the evolution of charge distribution as a function of time has been studied. Figure 9 shows the time dependence for both samples. The as-pressed XLPE shows heterocharge while the xylene-extracted XLPE shows homocharge. The magnitude of the charge in both samples increases with time. No sudden change of the polarity of charge is found in either samples.

Charge distributions at elevated temperatures have not been obtained because of instrumental limitations. All data shown in this report were obtained at room temperature. However, the effect of temperature on the formation of space charge should be considerable, in the sense that the charge mobility as well as the polymer chain mobility should be enhanced at elevated temperatures. A study of the temperature effect is needed.

The contribution of the components of XLPE to the formation of space charge can be summarized as follows:

1. Homocharge is accumulated in the pure crosslinked part of XLPE,

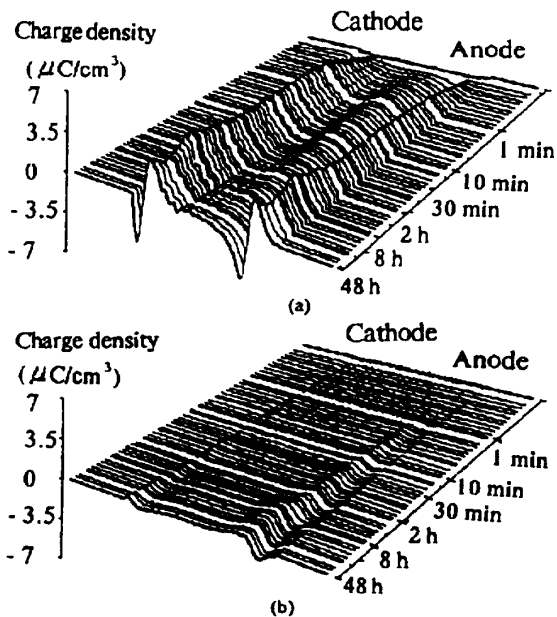


Figure 9.

Evolution of charge distribution at 21 kV for up to 48 h (a) As-pressed XLPE, (b) Xylene-extracted XLPE.

2. the non-crosslinked LDPE encourages the formation of heterocharge, but its effect is not strong,
3. the additive (antioxidant: Santanox R) prohibits the formation of heterocharge,
4. the residual byproducts encourage the formation of heterocharge, and
5. residual byproducts impose the most pronounced influence on the formation of space charge, so that only heterocharge is seen in an as-pressed XLPE with semi-conductive electrodes.

## REFERENCES

- [1] Y. Shao, K. Sheu, D. H. Damon, S. J. Huang and J. F. Johnson, "Dielectric Strength of Crosslinked Polyethylene: The Effects of the Volatile Products of the Crosslinking Reaction", Proc. CEIDP, pp. 465-470, 1989.
- [2] C. R. Lee, *Effects of Conditions of Semiconductive Electrodes on Electrical Conduction Characteristics of XLPE*, Master Thesis, Korea University, Seoul, Korea, 1992.
- [3] K. S. Suh, C. R. Lee and M. K. Han, "Electrical Conduction of XLPE with Vacuum Degassed Semiconductive Electrodes", Proc. CEIDP, pp. 130-135, 1992.
- [4] M. Nawata, H. Kawamura and M. Ieda, "Effects of Additives on dc Treeing Breakdown in Polyethyl-

- ene under Divergent Fields”, *IEEE Trans. Electr. Insul.*, Vol. 25, pp. 527–534, 1990.
- [5] N. Fukushi, “Effects of Additives on the Thermally Stimulated Current in Polyethylene”, *Proc. 5th Int. Symp. Electrets*, pp. 163–166, 1985.
- [6] F. Chapeau, C. Alquie, J. Lewiner, H. Auclair, Y. Pelet and R. Jocteur, “The Pressure Wave Propagation Method for the Analysis of Insulating Materials: Application to LDPE Used in HV Cables”, *IEEE Trans. Electr. Insul.*, Vol. 21, pp. 405–410, 1986.
- [7] H. Kon, Y. Suzuoki, T. Mizutani, M. Ieda and T. Suzuki, “Study of Space Charge in Polyethylene for Cable Insulation by Laser-induced-pressure-pulse Technique”, *Proc. 25th Symp. Electr. Insul. Matls*, pp. 421–424, 1993.
- [8] K. S. Suh, J. Y. Kim and M. K. Han, “Effects of Antioxidants on the Charge Formation in PE”, *Proc. 25 th Symp. Electr. Insul. Matls*, pp. 341–344, 1993.
- [9] M. Ieda, “Electrical Conduction and Carrier Traps in Polymeric Materials”, *IEEE Trans. Electr. Insul.*, Vol. 19, pp. 162–178, 1984.
- [10] Y. Li, M. Yasuda and T. Takada, “Influence of Crosslinking Residues on Spatial Charge Distribution”, *Proc. 3rd ICPADM*, pp. 1210–1213, 1991.
- [11] K. Kircher, *Chemical Reactions in Plastic Processing*, Hanser, Munich, pp. 159–160, 1987.
- [12] T. Ditchi, C. Alquie, J. Lewiner, E. Favrie and R. Jocteur, “Electrical Properties of Electrode/Polyethylene/Electrode Structures”, *IEEE Trans. Electr. Insul.*, Vol. 24, pp. 403–408, 1989.
- [13] K. S. Suh, E. J. Kim, M. K. Han and T. Takada, “Charge Accumulation Characteristics in XLPE with Heat Treated Semiconductive Electrodes”, *Proc. 4th ICSD*, pp. 418–422, 1992.
- [14] T. Takada, T. Maeno and H. Kushibe, “An Electric Stress-pulse Technique for the Measurement of Charges in Plastic Plate Irradiated by an Electron Beam”, *IEEE Trans. Electr. Insul.*, Vol. 22, pp. 497–501, 1987.
- [15] T. Maeno, T. Futami, H. Kushibe, T. Takada and C. M. Cooke, “Measurement of Spatial Charge Distribution in Thick Dielectrics Using the Pulsed Electroacoustic Method”, *IEEE Trans. Electr. Insul.*, Vol. 23, pp. 433–439, 1988.

*Manuscript was received on 19 July 1993, in final form 31 May 1994.*