PE/Ionomer 블렌드의 전하 Trapping 기구

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Charge Trapping Mechanisms of PE/Ionomer Blends

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요 약 : 열자극전류법을 이용하여 저밀도 폴리에틸렌/아이오노머 블렌드의 전하트랩기구를 조사하였다. -50℃에서 100℃까지의 온도범위에서 열자극전류 특성을 측정한 결과, 이 블렌드는 두 개의 열자극전류 피크를 갖는 것으로 관찰되었다. -5℃에서 10℃ 사이에서 나타나는 β 피크에 대한 특성을 분석한 결과 이 피크는 아이오노머 성분에서 유입된 쌍극자의 배열에 의한 피크인 것으로 보인다. 60℃ 이상에서 나타나는 α 피크는 비정질과 결정질 영역의 경계지역에 트랩되어 있는 주입전자에 의한 것으로 보인다. α 피크는 다시 온도순으로 α_1 및 α_2 두 개의 피크로 되어 있는데, α_1 피크는 이온성 경계에 그리고 α_2 피크는 에틸렌 경계에 트랩된 주입전자에 의한 것으로 판단된다. 또한 PE/Surlyn 1652 블렌드와 PE/Surlyn 1601 블렌드 모두 전하트랩 메카니즘은 동일한 것으로 판단된다.

Abstract : Charge trapping mechanisms of LDPE/Ionomer blends have been investigated using a thermally stimulated current(TSC) technique. Over the temperature range of -50 to 100℃, PE/ionomer blends show two peak, β and α peaks in the order of increasing temperature. The β peak which appears at -5 to 10℃ is associated with the orientation of dipoles originated from the ionomer component. The α peak which appears above 60℃ is associated with the electrons trapped at the interfaces between the amorphous and crystalline phases. This α peak is composed of two peaks, α_1 and α_2 peaks in the order of increasing temperature, which have different origins : α_1 peak is associated with the ionic interfaces and α_2 peak with the ethenic interfaces. The present results indicate that the trapping mechanisms for all TSC peaks seem to be the same for both PE/ Surlyn 1652 blends and PE/Surlyn 1601 blends.

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INTRODUCTION

Since the low density polyethylene in itself or in a crosslinked form is being used as a major insulation material for power cables, it is of great concern to improve the insulation performance of polyethylene. Various methods such as taping a good insulating film, filling inorganic fillers, or copolymerizing the ethylene with some comonomers have been proposed for this purpose.[1~3] Of these, a blending technique is quite promising because PE blends can be easily manufactured simply by conventional processing equipments.

It has been reported that the impulse breakdown strength of polyethylene may be improved by blending the ionomer which has inherent positive charges.[4] It is also known that the electric field dependence of total amount of charge is different depending on the type of ionomers.[5] For example, the total amount of charge in Surlyn 1652 which is neutralized with the zinc ions exhibited a monotonic increase with the electric field, whereas that in Surlyn 1601 which is neutralized with the sodium ions exhibited a considerable decrease at high fields.

In the case of incompatible blends, the more interfaces are introduced the more sites which can trap the charges are available, with the net result being an increase of total amount of charge. In this sense, the charge behavior, i.e. a decrease of total amount of charge at high fields, of Surlyn 1601 blends is quite interesting. A decreased amount of charge at high fields is quite promising in terms of improving the insulation reliability because it can reduce the possibility of dielectric breakdown caused by the accumulated space charges. Therefore, the differences in charge behavior in PE/ionomer blends may have to be investigated.

In the light of this background, the present work was centered at the investigation of charge trapping mechanisms in PE/ionomer blends using a thermally stimulated current(TSC) technique, as a part of efforts to understand the different charge behavior depending on the type of ionomers.

EXPERIMENTAL

PE/Ionomer blends were prepared from LDPE and ionomers. The polyethylene is being used as a raw material for the medium voltage power cable insulation. The ionomers used in this study are essentially polyethylene with a small amount of methacrylic acid copolymerized randomly into the ethylene chain. The acid functions are partially neutralized into a sodium (Surlyn 1601) or zinc (Surlyn 1652) salt. Table 1 contains the specification of Surlyn ionomers.

Table 1. Specification of Surlyn 1652* and Surlyn 1601*

Ionomer	Ion Type[1]	Melt Index[2]	% MAA[3]	% Neutralization[4]
Surlyn 1652	Zn	5.4	8.7	18
Surlyn 1601	Na	1.3	10.0	53

1 : type of cation, 2 : g/10 min, 3 : nominal % methacrylic acid, 4 : approximate % neutralization, * : Du Pont's ionomers

Blends were prepared by a plasticating extruder with a single screw. Temperatures at screw and die were set at 180 ℃. The blend ratios were typically 5, 10, 20, 50, and 80% by weight of ionomer. Typically 1 mil thick films were compression molded using a Carvor Laboratory Press at 180 ℃ for 10 min. Then gold electrodes were vacuum evaporated on both surfaces of film.

The wiring diagram shown in Fig. 1 indicates that the sample can be connected to a poling voltage, bias voltage, or ground. Both sides of film are in contact with the disc type electrodes which are electrically isolated from the temperature controlling device by 1 mm thick ceramic(Boron Nitride) disc. A resistive heater is placed on each side followed by a cooling disc with grooves inside. All parts were installed in a vacuum chamber so that the environment can be controlled.

Measurements of the TSC were made as follows :
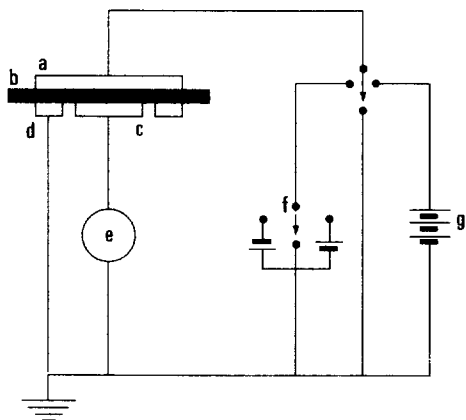
(1) The specimen was heated up to the poling

Fig. 1. Wiring diagram of the TSC apparatus ; a : counter electrode, b : sample, c : measuring electrode, e : electrometer, f : bias voltage, g : dc power supply.

temperature, typically 70 ℃.

(2) After the temperature was stabilized, the poling voltage was applied for the poling time, typically 20 min.

(3) After 20 min., the specimen was cooled, by circulating the liquid nitrogen through cooling discs, down to typically -80 ℃ with the voltage on.

(4) After the temperature was stabilized, the poling voltage was turned off and the transient current was removed.

(5) Then, the specimen was heated at a fixed heating rate and the TSC generated by the release of trapped charges was measured through an electrometer.

RESULTS AND DISCUSSION

TSC Thermograms of PE/Ionomer Blends

TSC thermograms for PE/Surlyn 1652(80/20) blend are shown in Fig. 2. In case of PE/Surlyn 1652 blend, one peak appears at around -5 ℃ (hereafter called β peak) and the other above 60 ℃ (hereafter called α peak). The TSC increases as the poling field increases, which holds true for both β and α peaks. There is also some shift in α peak temperatures as a function of poling field.
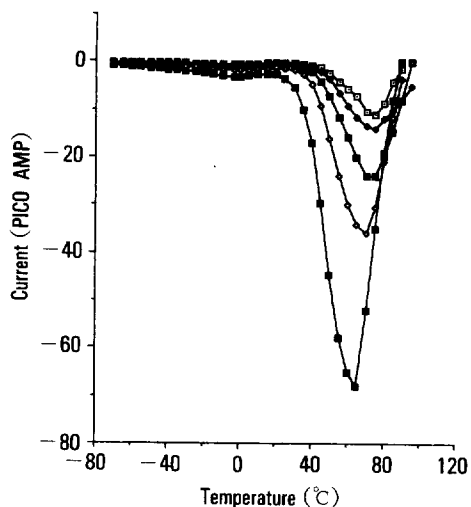

Fig. 2. Thermally stimulated currents of PE/Surlyn 1652 (80/20) blend : Poling conditions : 70 ℃, 20 min, +4.8 kV/mm (□), +8 kV/mm (◆), +12 kV/mm (◨), +16 kV/mm (◇), +28 kV/mm (■). Evaporated Au electrode.

When Surlyn 1601 was blended, two peaks, one at about 10 ℃ (hereafter called β peak) and the other at about 80 ℃ (hereafter called α peak), were observed(Fig. 3). The β peak current increases as the poling field increases. A poling field dependence of α peak current of the PE/Surlyn 1601 blend, the α peak current increases at low poling fields but decreases at high fields above roughly +10kV/mm.

For both blends, the α peak seems to be composed of two peaks. These are assigned as α_1 and α_2 in the order of increasing temperature.

Assignment of β Peaks

The assignment of β peak observed at -5 to 10 ℃ is relatively simple. The β peak currents of PE/Surlyn 1601 blends were plotted against both poling fields (a) and ionomer concentrations (b) in Fig. 4. The features which can be found in the figure are (1) the β peak current is directly proportional to the poling field, (2) the β peak current is also directly proportional to the ionomer content, and (3) the β peak current passes through the original point (0, 0) in a plot of the peak cur-

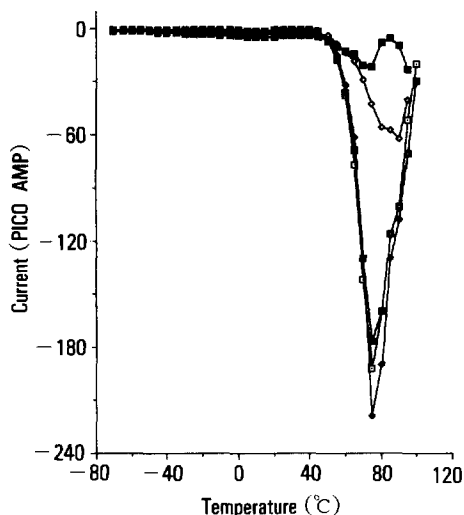Kwang S. Suh, Eunjoo Kim, John Tanaka, and Dwight H. Damon

Fig. 3. Thermally stimulated currents of PE/Surlyn 1601 (80/20) blend : Poling conditions : 70℃, 20 min, +8 kV/mm (⊡), +12 kV/mm (◆), +16 kV/mm (◘), +28 kV/mm (◇), +37 kV/mm (■). Evaporated Au electrode.

rent vs. poling field and ionomer content. Similar features were found in PE/Surlyn 1652 blends.

These features are the direct evidences for the dipolar orientation.[8,9] It is well documented in the literature that in the case of dipolar orientation mechanism the peak current, i_m, is directly proportional to the poling field, E_p, and that i_m vs. E_p plot passes $(0, 0)$. Also, the β peak seems to originate from the dipoles of the ionomer component. The reason for this is that the β peak current is directly proportional to the ionomer content. The β peak of ethylene-based ionomers is well known to arise from the micro-Brownian motion of -COOM or -COOH functional groups in ethylene methacrylic acid (EMA)-substituted region.[10~12]

Effect of Collecting Voltages on α Peaks

In many cases, two α peaks were observed in the present study. These were assigned in the above as α_1 and α_2 in the order of increasing temperature. In order to differentiate the origins of these peaks, the effect of collecting voltages on α peaks was investigated.
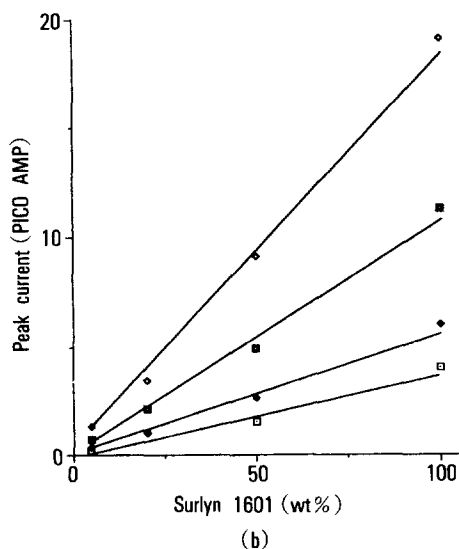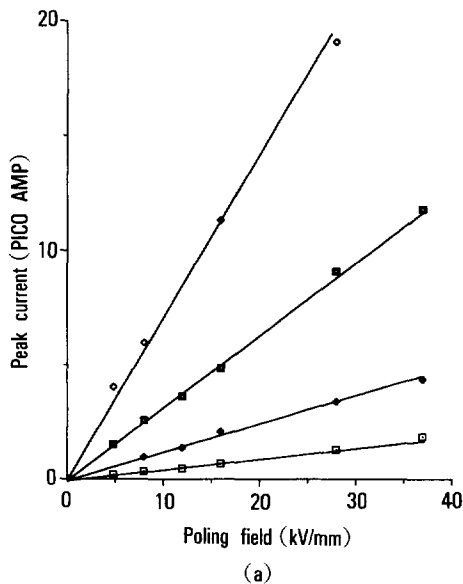

(a)

(b)

Fig. 4. (a) Effect of poling field on the β peak current of PE/Surlyn 1601 blends : Wt % of Surlyn 1601 : 5 (⊡), 20(◆), 50(◘), 100(◇). (b) Effect of ionomer concentration on the β peak current of PE/Surlyn 16 01 blends : Poling fields : +4.8 kV/mm (⊡), +8 kV/mm (◆), +16 kV/mm (◘), +28 kV/mm(◇).

A collecting voltage is the voltage applied to the sample when the polarized charges are released by the thermal motion of polymer chains. Changes caused by the application of collecting voltage can

be used as a measure of the interaction of trapped charges (electrons in the case of polyethylene) with the traps at the trapping sites. In an electronic process, the extent of change can be used as a measure of how tightly the charges are bounded with the traps. In other words, when the electrons are loosely bounded the polarity reversal of resultant TSC is expected under collecting voltage, whereas when tightly bounded a change only in magnitude is expected.

Figure 5 shows the effect of collecting voltage on the TSC of PE/Surlyn 1652(80/20) blend. As shown in Fig. 5, when only 5% of poling field (+0.8 kV/mm) was applied as a collecting voltage, the α peak was observed at about 60℃ with a sharp change of current afterward and finally the polarity of α peak was reversed from - to +. As the collecting voltage increases up to 20% of poling field(+3.2 kV/mm), the current magnitude for the α peak decreases and then the current changes sharply towards the positive polarity. When the reverse collecting voltage is applied

(-1.6 kV/mm), the polarity of α peak was not changed. These features are the typical ones for all other PE/Surlyn 1652 blends and PE/Surlyn 1601 blends.

It is clear from these results that the origins for α_1 and α_2 peaks are different : α_1 peak is associated with the charges bounded tightly with the traps and α_2 peak with the charges bounded loosely with the traps. Its electrical implication is that the electrons associated with the α_1 peak have some degree of electrical interaction with the traps and the α_2 peak without any electrical interaction but just a physical trapping with the traps.

Work Functions and Activation Energy of α Peak

Characteristics of α peaks were further analysed using two methods : One is the work function dependence of α peak current and the other an estimation of activation energy for the α peak using a so-called initial rise method. These works were carried out to get the information on the origin of α peaks.

Figure 6 shows that the α peak current of all samples declines as the work function increases, which means that the more difficult it is to emit
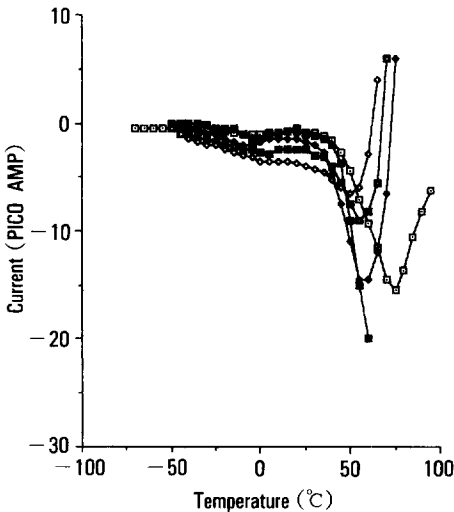
Fig. 5. Effect of collecting voltages on the TSC of PE/Surlyn 1652(80/20) blend : Poling field : +16 kV /mm, collecting voltage : 0 kV/mm (⊡), +0.8 kV/mm (◆), +1.6 kV/mm (◘), +3.2 kV/mm (◇), -1.6 kV /mm(■).
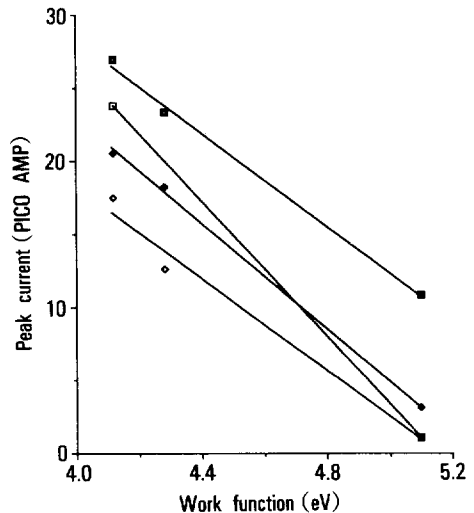
Fig. 6. α peak current of PE/Surlyn 1652 blends as a function of work function : Wt% of Surlyn 1652 : 0 (⊡), 5(◆), 20(◘), 100(◇).

the electrons from the electrode, the fewer electrons are injected into the polymer. An activation energy associated with the α_1 peak was estimated from an initial rise method to be about 1.3 eV for PE/Surlyn 1652 blends as shown in Fig. 7. Similar features were observed in PE/Surlyn 1601 blends.

Assignment of α Peak

The results shown in Figs. 6 and 7 are very informative in assigning the origin of α peak. The work function is defined as an energy required to excite the electrons from Fermi energy level to the conduction band. The work function at a fixed condition governs the amount of electrons emitted from the electrode and injected into the sample. Therefore, the peak current associated with the electron injection mechanism decreases as the work function of electrode increases. It is known that an activation energy of 1.3 eV corresponds to the trap depth associated with the interfaces between the amorphous and crystalline phases in polyethylene.[11~13] Also, the dynamic mechanical analysis has indicated that the chain relaxation of polyethylene at the temperatures above roughly 50 °C is associated with the relaxation of crystalline phases.[14,15] Therefore, it can be concluded that the α peak arises from the electrons trapped at the interfaces between the amorphous and crystalline phases.

However, since the α peak can be frequently resolved into two peaks, it needs to be further discussed. Since a base material for the ionomer is a random copolymer of ethylene and methacrylic acid, crystalline phases of ionomer are composed mainly of ethylene chains. Ionic clusters which are the aggregations of ion pairs may exist dominantly at the interfaces between the amorphous and crystalline phases. Then, these interfaces can be reduced into 2 parts ; one with and the other without "ionic interfaces". Here, the "ionic interfaces" is defined as the interfaces associated with the ionic clusters and the "ethenic interfaces" as those associated only with ethylene chains. In this situation the electrons will be bounded more strongly with the ionic interfaces than with the ethenic in
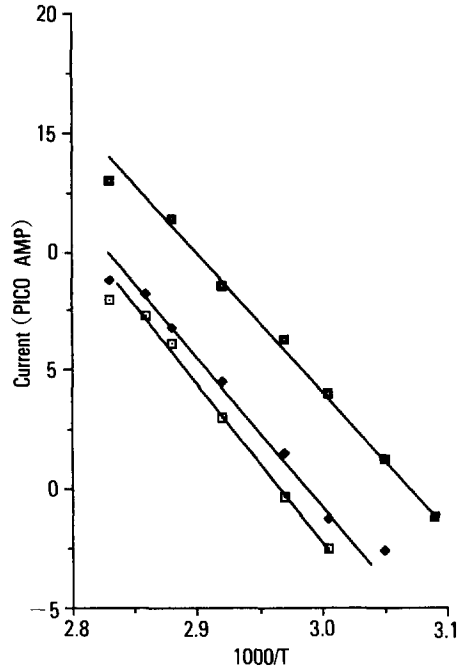

Fig. 7. Initial rise current of PE/Surlyn 1652 (80/20) blend at several poling fields : Poling field : $+4.8$ kV /mm(▣), $+8$ kV/mm(◆), $+11.5$ kV/mm(◩).

terfaces.

On these bases, it can be concluded that the α_1 peak is associated with the electrons trapped at ionic interfaces and the α_2 peak is associated with ethenic interfaces, both being related to the interfaces between the amorphous and crystalline phases. This assignment seems to hold true for both PE/Surlyn 1652 blends and PE/Surlyn 1601 blends, because no clear differences in all features observed were found in both blends.

CONCLUSIONS

Conclusions on the charge trapping mechanisms of PE/Ionomer blends by measuring TSC characteristics are as follows :

(1) Over the temperature range of -50 to 100 °C, two TSC peaks, β and α in the order of increasing temperature, are observed in PE/ionomer blends.

(2) β peaks are observed at about -5 °C for PE

/Surlyn 1652 blends and about 10℃ for PE/Surlyn 1601 blends. α peaks observed above 60℃ are composed of two peaks, α_1 and α_2 in the order of increasing temperature.

(3) β peak is associated with the orientation of dipoles originated from the ionomer component. α_1 peak is associated with the electrons trapped at ionic interfaces and α_2 peak at ethenic interfaces, both being related to the interfaces between amorphous and crystalline phases.

(4) Trapping mechanisms seem to be the same for both PE/Surlyn 1652 blends and PE/Surlyn 1601 blends.

REFERENCES

1. T. Tanaka, *IEEE PES Summer Meeting, July 18-23,* 1976.

2. M. Ikeda and Y. Ohki, "2nd Int. Conf. on Cond. and Breakdown in Solid Dielectr.", Erlangen, Germany, 71, 1986.

3. T. Kawashima, T. Maki, T. Takahashi, and K. Maeda, *Proc. 3rd Int. Conf. Prop. Appli. of Dielectr. Mater.,* July 8-12, Tokyo, Japan, 222 (1991).

4. H. Fugakawa and Y. Yasuo, *Comm, BIII-2, J'Cable 84,* 283 (1984).

5. K. S. Suh, PhD Dissertation, University of Connecticut, USA, 1987.

6. J. Van Turnhout, "Topics in Applied Physics", Edt. by G. M. Sessler, Springer-Verlag, Berlin, Vol. 33, Chapter 3, 1980.

7. C. Bucci, R. Fieschi, and G. Guidi, *Phys. Rev.,* **148,** 816 (1966).

8. P. J. Philips and W. J. MacKnight, *J. Polym. Sci., Part A-2,* **8,** 727 (1970).

9. S. Yano, H. Yamashita, M. Matsushita, A. Aoki, and J. Yamanchi, *Colloid & Polym. Sci.,* **259,** 514 (1981).

10. J. Vanderschueren, J. Niezette, and R. Vanderschueren, *J. Polym. Sci., Polym. Lett. Ed.,* **21,** 799 (1983).

11. M. Ieda, *IEEE Trans. Electr. Insul.,* **EI-19,** 162 (1984).

12. T. Hashimoto, M. Shiraki, and T. Sakai, *J. Polym. Sci., Polym. Phys. Ed.,* **13,** 2411 (1975).

13. D. K. Davis, *J. Phys. D,* **5,** 162 (1972).

14. Y. P. Khanna, E. A. Turi, T. J. Taylor, V. V. Vickroy, and R. F. Abbott, *Macromolecules,* **18,** 1302 (1985).

15. R. Popli, M. Glotin, R. Mandelkern, and R. S. Benson, *J. Polym. Sci., Polym. Phys. Ed.,* **22,** 407 (1984).