

PE/Ionomer 블렌드의 열자격전류

Thermally Stimulated Currents of PE/Ionomer Blends

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Abstract - The behavior of space charge in PE/ionomer blends has been investigated using the thermally stimulated current(TSC) technique. In the blends, at least two TSC peaks over the temperature range from -50 to 100°C are observed, one at -5 ~ 10°C (β peak) and the others at above 60°C (α peak). The β peak is assigned as the orientation of dipoles from the ionomer component. Two α peaks seem to be related to the charge trapping at sites related to the crystalline phases. One α peak is associated with the ionic interfaces and the other with the ethylene chains without the ionic interfaces. The amount of charges stored in PE/Surlyn 1652 blends increases as the poling field increases over the field range of +8 ~ +30 kV/mm, whereas that in PE/Surlyn 1601 blends increases slightly at low poling fields and then decreases at high poling fields above +10 kV/mm. Exact reasons for such a difference are not known at this point.

1. INTRODUCTION

Low density polyethylene(LDPE), an important insulation material in the cable industry, is known to be negatively charged mainly due to the injection of homocharges from the metal conductor. In dc cables, the accumulated negative charges(space charges) may result in a sudden dielectric failure when a sudden polarity reversal occurs. Such transient conditions can be achieved by such phenom-

ena as lightning strike or switching surge. The injection of homocharges from the metal into the insulation material is unavoidable as long as the voltage is applied across the polyethylene. Therefore, an increase in reliability of cable insulation can be achieved by reducing the accumulation of space charges.

The behavior of space charges in polyethylene with low molecular weight species such as various additives, NaCl, CuCl₂, I₂[1-4] and with the bulky polymers[5] has been extensively studied. Generally it is known that the presence of impurities in the pure polyethylene increases the amount of space charge and hence decreases the

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dielectric breakdown strength. However, a recent study has reported that the impulse breakdown strength of polyethylene may be improved by blending polyethylene with an ionomer which has inherent positive charges[6] and electrifies positively[7]. This observation is somewhat contradictory to the previous concept that the blending decreases the dielectric breakdown strength by introducing more charges. Therefore, the behavior of space charge in PE/ionomer blends has to be investigated for a better understanding of the correlation between the impulse breakdown strength and space charge.

In this report, therefore, the behavior of space charges in PE/ionomer blends investigated using a thermally stimulated currents(TSC) technique is described. In this study, two ionomers, Surlyn 1652 and Surlyn 1601, were separately evaluated.

2. Experimental

PE/Ionomer blends were prepared from LDPE (Union Carbide, Grade#6201) and ionomers(Du Pont's Surlyn). This 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. An interesting feature in ionomers is that the ion pairs in neutralized sites exist as an "ionic cluster" which is an aggregation of ion pairs. These ionic clusters act to "cross-link" the polymer resulting in a very tough product. Table 1 contains the specification of Surlyn ionomers.

Blends were prepared by a plascating extruder with a single screw made by Wayne Machine & Die Co. Temperatures at screw and die were set at

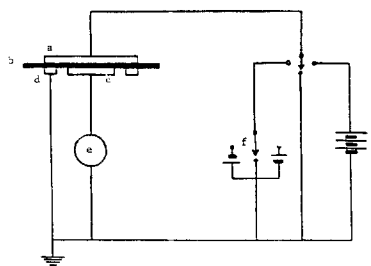


Fig. 1 Wiring diagram of the TSC apparatus : a : counter electrode, b: sample, c: measuring electrode, e: electrometer, f: bias voltage, g: dc power supply.

180°C. The screw speed was set at 20rpm, and with that speed the pressure was recorded between 1000 to 1100 psi. The blend ratios were typically 0, 5, 10, 20, 50, 80 and 100% by weight of ionomer for both Surlyn 1601 and Surlyn 1652. Typically 1 mil thick films were compression molded using a Carver Laboratory Press at 180°C for 10 min. Then gold electrode was deposited on the surface of film by a vacuum evaporator.

The wiring diagram shown in Fig. 1 indicates that the sample can be connected to a poling voltage, bias voltage, or ground. The direction of poling for poling voltage or bias voltage can also be selected. Both sides of film are in contact with the disc type electrodes which are electrically isolated from the temperature controlling device by one millimeter thick ceramic (Boron Nitride) disc. A resistive heater is then placed on each side followed by cooling coils. Typical experimental conditions are as follows: Poling temperature (T_p): 70°C, Poling time (t_p): 20 min., Poling field (E_p): +8 kV/mm, Heating rate (R_h): 5°C/min., Temperature at $E_p=0$ (T_0): -50°C, and Time at T_0 (t_0): 30 min.

3. Results and Discussion

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

3.1 Typical TSC thermograms

TSC thermograms for pure polyethylene and PE/Surlyn 1652(80/20) blend are shown in Fig. 2 and 3, respectively. In general, the TSC peaks increase as the poling field increases. There is also some shift in the peak temperature as a function of poling field. There are clearly one peak (hereafter β peak) at around -5°C and at least one peak (hereafter α peak) above 60°C . In the case of pure LDPE, positive β peaks are observed, but

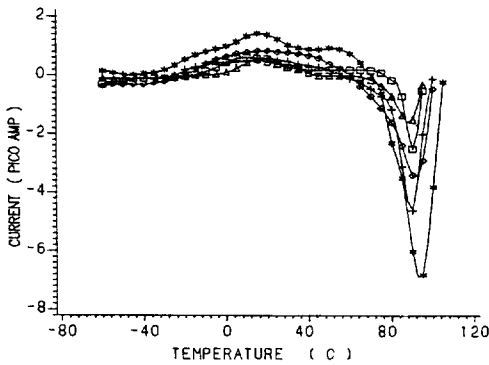


Fig. 2 Thermally stimulated currents of polyethylene : Poling conditions : 70°C , 20 min, +4.8 kV/mm (Δ), +8 kV/mm (\square), +12 kV/mm (\diamond), +16 kV/mm (+), +20 kV/mm (*), Evaporated Au electrode.

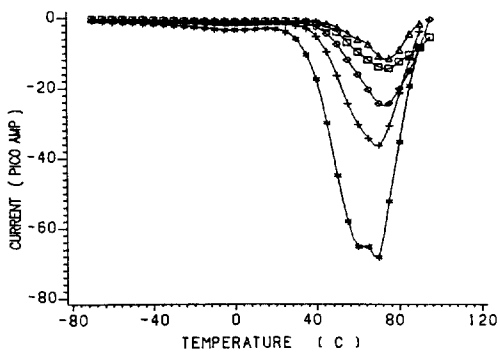


Fig. 3 Thermally stimulated currents of PE/Surlyn 1652(80/20) : Poling conditions : 70°C , 20min, +4.8 kV/mm (Δ), +8 kV/mm (\square), +12 kV/mm (\diamond), +16 kV/mm (+), +28 kV/mm (*), Evaporated Au electrode.

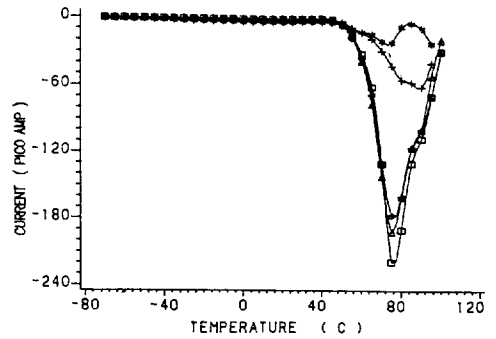


Fig. 4 Thermally stimulated currents of PE/Surlyn 1601(80/20) : Poling conditions : 70°C , 20min, +8 kV/mm (Δ), +12 kV/mm (\square), +16 kV/mm (\diamond), +28 kV/mm (+), +37 kV/mm (*), Evaporated Au electrode.

they disappear when the ionomer was added. It can be seen that the addition of Surlyn 1652 increases the peak current and shifts the peak temperature to the lower temperatures. The β peaks show changes only in magnitude of current without any change in peak temperatures.

When Surlyn 1601 is blended, on the other hand, the observed features are somewhat different from those in PE/Surlyn 1652 blends as shown in Fig. 4. In this case, β peak was observed around 10°C , whereas two α peaks, one at about 80°C and the other at about 90°C were observed. The β peak current increases with the poling field. A major difference from PE/Surlyn 1652 blends is that the α peak current increases at low fields but decreases at high fields above roughly +10 kV/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.

3.2 Low temperature(β) peak

The β peak current for PE/Surlyn 1601 blends was plotted against the poling field (Fig. 5) and the ionomer concentration (Fig. 6). For all blends the linear relationship is retained and all pass through the original point(0, 0) in a plot of peak current vs. poling field as well as in a plot of peak current vs. ionomer concentration as the

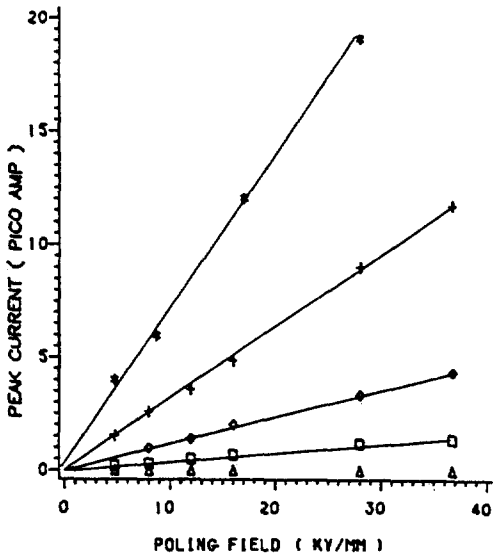


Fig. 5 Effect of poling field on the β peak current of PE/Surlyn 1601 blends: *Wt%* of PE/Surlyn 1601 : 100/0(Δ), 95/5(\square), 80/20(\diamond), 50/50(+), 0/100(*).

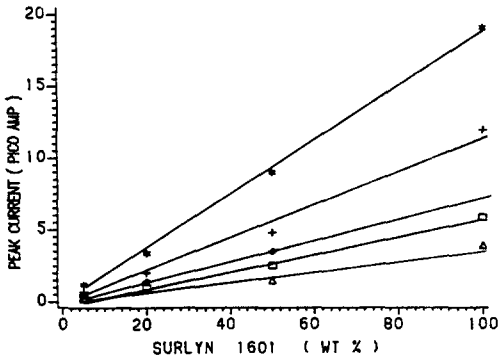


Fig. 6 Effect of ionomer concentration on the β peak current of PE/Surlyn 1601 blends: Poling fields: +8 kV/mm(Δ), +12 kV/mm(\square), +16 kV/mm(\diamond), +28 kV/mm(+), +37 kV/mm(*).

poling field and ionomer concentration approach zero. The β peak current of PE/Surlyn 1652 blends follows the same trend as that of PE/Surlyn 1601 blends. The only difference between the two is the magnitude, PE/Surlyn 1601 having a higher magnitude in peak current than PE/Surlyn 1652 blends. No change in β peak temperature was observed for both PE/Surlyn 1652 and PE/

Surlyn 1601 blends.

3.3 Effect of poling field and ionomer concentration on the α peak current.

The observed α peak current was plotted against the poling field on a double logarithmic scale in Fig. 7 for PE/Surlyn 1652 blends and in Fig. 8 for PE/Surlyn 1601 blends. For PE/Surlyn 1652 blends, a linear family of curves in a log i vs. log E plot is observed, so that the α peak current as a function of the poling field follows a power law. For PE/Surlyn 1601 blends, a different trend was observed. With 5% of Surlyn 1601, the peak current decreases over the field range of +8 ~ +30 kV/mm. With 20% of Surlyn 1601, the peak current increases at low poling fields and then decreases at high poling fields above about +10 kV/mm. For example, the peak current of 20% of Surlyn 1601 is lower by a factor of 1/6 at +28 kV/mm than that at +8 kV/mm.

The α peak current as a function of ionomer concentration is shown in Fig. 9 for PE/Surlyn

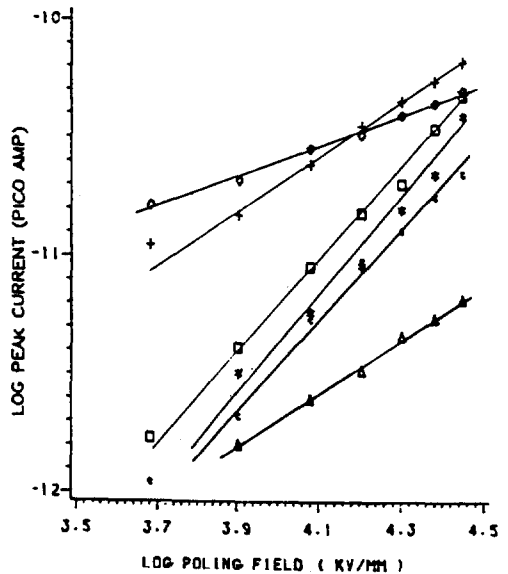


Fig. 7 Effect of poling field on the α peak current of PE/Surlyn 1652 blends: *Wt%* of PE/Surlyn 1652 : 100/0(Δ), 95/5(\square), 90/10(\diamond), 80/20(+), 50/50(*), 0/100(\circ).

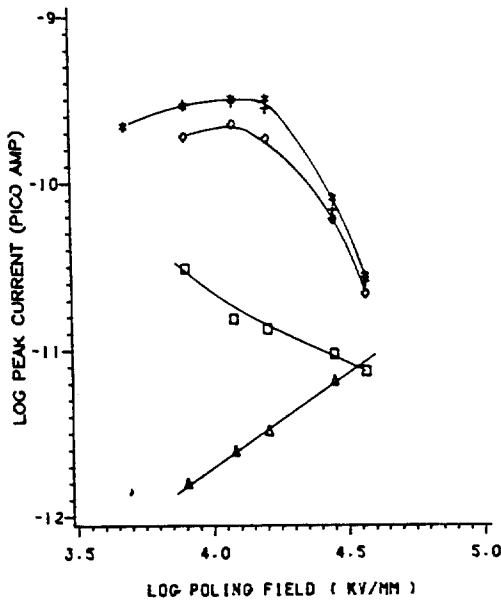


Fig. 8 Effect of poling field on the α peak current of PE/Surlyn 1601 blends: *Wt%* of PE/Surlyn 1601 : 100/0(Δ), 95/5(\square), 80/20(\diamond), 50/50(+), 0/100(*).

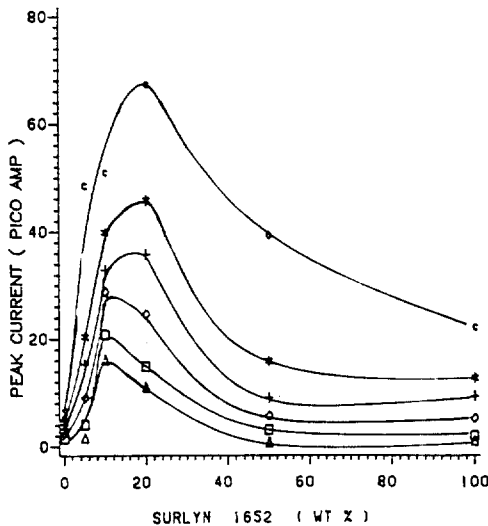


Fig. 9 Effect of poling field on the α peak current of PE/Surlyn 1652 blends: Poling fields: +4.8 kV/mm(Δ), +8 kV/mm(\square), +12 kV/mm(\diamond), +16 kV/mm(+), +24 kV/mm(*), +28 kV/mm(\circ).

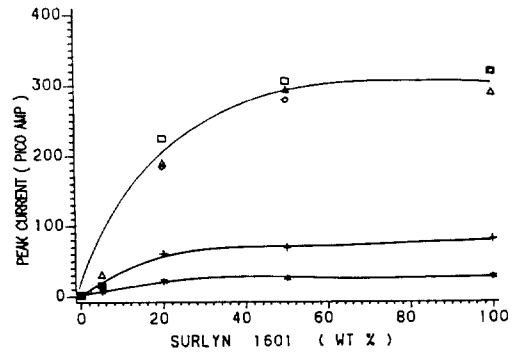


Fig. 10 Effect of poling field on the α peak current of PE/Surlyn 1601 blends: Poling fields : +8 kV/mm(Δ), +12 kV/mm(\square), +16 kV/mm(\diamond), +28 kV/mm(+), +37 kV/mm(*).

1652 blends and in Fig. 10 for PE/Surlyn 1601 blends. As the concentration of Surlyn 1652 increases until it is pure Surlyn 1652, the α peak current passes through a maximum. The blends containing less than 50% of Surlyn 1652 show larger peak current than the pure Surlyn 1652. A maximum occurs at 10~20% of Surlyn 1652. In the case of Surlyn 1601, however, no such maxima in a plot of α peak current vs. ionomer concentration is observed. With 20% or more of Surlyn 1601, the current observed is almost the same as that of pure Surlyn 1601. At low poling fields, the currents of PE/Surlyn 1601 blends are much higher than those of PE/Surlyn 1652 blends. At high poling fields, however, the currents of PE/Surlyn 1601 blends are smaller than those of PE/Surlyn 1652 blends. For example, the peak current of 20% of Surlyn 1601 is higher by a factor of about 10 at +8 kV/mm, but lower by a factor of about 0.2 at +28 kV/mm than that of 20% of Surlyn 1652 at comparable fields.

3.4 Discussion

Thermally stimulated currents of various PE/ionomer blends have shown the two major features, the first one being related to the identification of the origins for the observed peaks and the second one to the differences in the behavior of space charge depending on the type of ionomer :

- (1) Two peaks were observed in the temperature range of -50 to 100°C . The β peaks were observed in the temperature range of -5 to 10°C depending on the type of ionomer and α peaks at the temperature above 60°C . In most cases, the α peak seems to be composed of two peaks, α_1 and α_2 in the order of increasing temperature.
- (2) The TSC of blends with Surlyn 1652 increases as the poling field as well as the ionomer content increases, whereas that with Surlyn 1601 decreases at the high poling fields above roughly $+10$ kV/mm. Note that in the case of 5% of Surlyn 1601, the TSC decreases monotonically

First of all, the assignment of β peak observed at -5 to 10°C is relatively simple. Regarding this, the following four observations are informative: (1) the β peak current is directly proportional to the poling field, (2) the β peak current is also directly proportional to the concentration of ionomer, (3) the β peak current passes through the original point (0, 0) in a plot of the peak current vs. poling field and ionomer content, and finally (4) the β peak temperature stays unchanged regardless of the experimental variables such as poling field and the ionomer content. These features are common to both types of ionomer. In the case of (4), however, PE/Surlyn 1601 blends exhibit a little bit higher peak temperature, by about 10 to 15°C , than PE/Surlyn 1652 blends. Of these, features (1) to (3) are the direct evidence for the dipolar orientation [8, 9]. It is well documented that 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). In the case of charge injection, however, the electric field has to be above a critical one above which the electrons are emitted from the metal electrode. 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 concentration. The β peak of ethylene-based ionomers is well-defined to arise from the micro-Brownian motions originating from $-\text{COOM}$ or $-\text{COOH}$ functional groups in EMA-substituted region [10~12]. Therefore, the β peak can be assigned to the

orientation of dipoles from the ionomer component.

On the other hand, the α peak seems to be associated with the charge trapping at the region related to the crystalline phases. 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 [13, 14]. The results on the TSC characteristics of polyethylene have also suggested that the TSC peak observed at the comparable temperature range is associated with the charge trapping at the interfacial region between the amorphous and crystalline phases [15~17]. In ionomers or PE/ionomer blends, there are three different types of interface: between the amorphous and crystalline phases, between the segregated ionomer and polyethylene domains, and between the ethylene chains and ionic clusters. It is very difficult to distinguish the contribution of each of these interfaces to the total polarization. Since the base material for the ionomer is the random copolymer of ethylene and methacrylic acid, the crystalline phases of ionomer are composed mainly of ethylene chains. Ionic clusters which is an aggregation of ion pairs exist dominantly at the amorphous region or at the interfaces between the amorphous and crystalline phases. Then, the interfaces can be reduced into 2 types; one with and the other without "ionic interfaces". Here, the ionic interfaces can be defined as the ones with the ionic interfaces. The trapping mechanism might be different when the injected charges are trapped at the ionic interfaces and when trapped at the ethylene chains without the ionic interfaces. On these bases, the result that two α peaks, α_1 and α_2 , are observed in many cases may suggest that one peak is associated with the ionic interfaces and the other with the ethylene chains, both being related to the crystalline phases. At this stage, however, the exact assignment for the α_1 and α_2 peaks are not available. Currently works are in progress to make this assignment clear.

Another important feature observed in the present study is that PE/Surlyn 1652 blends and PE/Surlyn 1601 blends exhibit the different poling field dependence of the α peak current. See Section

3.3 in Results and Discussion. The peak current can represent the amount of charge stored within the dielectric, provided the peak shape is approximately gaussian. Then, it can be said that the amount of charge stored in PE/Surlyn 1652 blends increases as the poling field increases, whereas that in Surlyn 1601 blends increases first but decreases at high poling fields above about +10 kV/mm. In the case of polyethylene as well as most insulators, it is general that, as the poling field increases, the resultant TSC increases due to the increased amount of trapped charge. In this sense, the increased TSC with the poling field in PE/Surlyn 1652 blends can be explained by a simple interfacial polarization concept. That is, the blends produced more defects or interfaces, so that the amount of charge trapped at those defective or interfacial sites increases as the poling field increases, the net result being an increase of the resultant TSC. Also, no interaction of injected charges with the ionic phases in the interfacial region is expected. In PE/Surlyn 1601 blends, on the other hand, the amount of charge stored decreases at high poling fields by some reason.

Speculating the reasons for this is not simple because Surlyn 1601 is different from Surlyn 1652 in such parameters at the % EMA (10 vs. 8.7%), the % neutralization (53 vs. 18%) and the type of ion (Na vs. Zn). The % EMA may not be a critical factor because only about one % is different. However, the effects of the % neutralization and the type of ion may not be excluded. Surlyn 1601 possesses the higher % neutralization and hence the larger amount of ionic cluster than Surlyn 1652. Then, it can be said that the more crosslink sites are available in Surlyn 1601 than in Surlyn 1652. In general, the crosslinking decreases the TSC because of reduced chain mobility. Also, it may be one of the reasons that, by some reason, Na ions may interact with the incoming charges so that the amount of charge stored within dielectric is reduced, whereas Zn ions do not. At this point, however, no further explanation is available.

This study was initiated, in part, to find the correlation between the amount of charge and the impulse breakdown strength of PE/ionomer

blends. Unfortunately, it is not possible with the present results to draw a good correlation between these parameters. The major reasons for this are that the TSC characteristics are quite different depending on the type of ionomer and that nothing is specified regarding the type of ionomer in Reference #6 where the improved impulse breakdown strength of PE/ionomer blends is described.

4. Conclusions

The results and discussion on the behavior of space charge in PE/ionomer blends lead to the following conclusions:

- (1) At least two TSC peaks over the temperature range of -50 to 100°C are observed, one at $-5\sim 10^{\circ}\text{C}$ (β peak) and the others at above 60°C (α peak). The β peak is assigned as the orientation of dipoles from the ionomer component. Two α peaks seem to be related to the charge trapping at sites related to the crystalline phases. One α peak is associated with the ionic interfaces and the other with the ethylene chains without the ionic interfaces.
- (2) The amount of charges stored in PE/Surlyn 1652 blends increases as the poling field increases over the field range of $+8\sim +30$ kV/mm, whereas that in PE/Surlyn 1601 blends increases slightly at low poling fields and then decreases at high poling fields above about +10 kV/mm. The exact reason for this difference is not known at this point.
- (3) No conclusive correlation between the impulse breakdown strength and the amount of space charge is available due to the different TSC characteristics depending on the type of ionomer described in (2).

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