

# Charge Behavior in Polyethylene-Ionomer Blends

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## ABSTRACT

In order to explain a decrease of thermally stimulated current (TSC) at high poling fields, the behavior of space charge in two types of polyethylene (PE)/ionomer blends, PE/Surlyn 1652 and PE/Surlyn 1601, has been investigated by measuring the charge distributions and conduction characteristics. PE/Surlyn 1601 blends showed smaller current densities at high electric fields than PE/Surlyn 1652 blends. A considerable amount of negative charge was found to migrate into the bulk region of PE/Surlyn 1601 blends upon discharging, which was attributed to the strong electron affinity of ionic clusters existing only in Surlyn 1601. This migration of charge made the charge distribution uniform, resulting in a decrease of TSC at high poling fields. This phenomenon was not found in PE/Surlyn 1652 blends.

## 1. INTRODUCTION

POLYMER blends are frequently used for improving the electrical properties of insulating materials. A typical example can be found in polyethylene/ionomer (PE/ionomer) blends designed for dc cable insulation. It has been reported that the impulse breakdown strength of polyethylene can be improved by blending with the ionomer. This has been attributed to the neutralization of injected negative charges by positive charges residing in the ionomer [1].

During a study on the thermally stimulated current (TSC) characteristics of these blends, quite interesting results have been observed on the poling field dependence of the TSC peak current [2, 3]. For example, the TSC peak current in PE/Surlyn 1652 blends increased monotonically as the poling field increased, whereas that in PE/Surlyn 1601 blends exhibited a considerable decrease at high poling fields. Here, Surlyn 1652 and Surlyn 1601 are DuPont's ethylene-based ionomers containing different metal cations.

It is generally accepted that in polyethylene a higher poling field results in a larger TSC because of an increased amount of trapped charge. The more interfaces are introduced in blends, the more trapping sites are available, resulting in an increase of total amount of charge and thus an increase of TSC. In this sense, the poling field dependence of TSC peak current in PE/Surlyn 1652 blends can be explained in terms of interfacial polarization [4].

However, the charge behavior of PE/Surlyn 1601 blends cannot be explained readily. Two speculations are possible. One is that the injected charge is neutralized by some species having opposite polarity. The other is that the injected charge is distributed uniformly throughout the specimen. A uniform distribution of charge results in a decrease in TSC.

Table 1. Specifications of Surlyn 1652 and Surlyn 1601 [5]. MI: Melt index (190°C, 2.16 kg), MAA: Nominal mole percentage of methacrylic acid.

Ionomer Surlyn	Ion type	MI g/10 min	MAA %	Neutr. %
1652	Zn <sup>2+</sup>	5.4	8.7	18
1601	Na <sup>+</sup>	1.3	10.0	53

In light of this background, the behavior of space charge in these two PE/ionomer blends has been investigated by measuring charge distributions and conduction currents. These results were used to explain the TSC behavior in the PE/ionomer blends described above.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. MATERIALS

PE/ionomer blends were prepared from PE and ionomers. The PE used in this study is being used as a raw material for medium voltage power cable insulation. Its density and melt index are 0.920 g/cm<sup>3</sup> and 2.0 g/10 min, respectively. The ionomers used in this study are essentially PE 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 used in this study [5]. Blends were prepared by a single screw plasticating extruder in which screw and die were set at 180°C. Blends were kept in a dessicator until the specimen was tested.

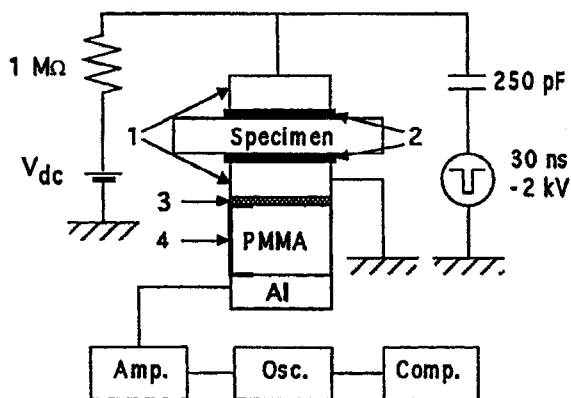


Figure 1. Schematic diagram of charge distribution measurement system: 1: Al electrode, 2: semicon electrode, 3: PVDF film, 4: Al tape.

## 2.2. CHARGE DISTRIBUTIONS

Charge distributions were measured by a pulsed electroacoustic (PEA) method, the schematic diagram of which is shown in Figure 1. It consists of an electric pulse generator (pulse width 90 ns, pulse height  $-1$  kV), HV source ( $+30$  kV<sub>dc</sub>), a test cell with a piezoelectric detector, and a data acquisition system. The piezoelectric detector was made of a 28  $\mu$ m thick poly (vinylidene fluoride) (PVDF) film because of its excellent wide band characteristics in the frequency domain. The data acquisition system consists of wide band preamplifier, digitizing oscilloscope and a personal computer. Details of measurement principles and techniques are described elsewhere [6, 7].

500 to 700  $\mu$ m thick specimens were compression molded at 180°C for 10 min.  $\sim 150$   $\mu$ m thick semicon electrodes were compression molded from a raw material used for the strand shield of power cables, and were attached onto both surfaces of the test specimen using a hot iron. The semicon electrode was a compound made of olefinic polymer, processing aids, conductive carbon black and antioxidants.

Up to 22 kV<sub>dc</sub> was applied to the specimen in a stepwise manner. In each step, the voltage was applied for 30 min and a charge distribution was obtained at the end of this period, while the voltage was being applied. The sample was then short circuited and another charge distribution was obtained. The delay time was  $< 3$  min. After all these processes had been completed, the voltage was ramped up to the next test voltage. The final voltage was 21.6 kV which corresponds to an electric field of 300 to 400 kV/cm.

## 2.3. CONDUCTION CURRENTS

Films  $\sim 40$   $\mu$ m thick were prepared by compression molding using a Carver Laboratory Press at 180°C for 10 min. We employed a semicon electrode made of the same type of material as used in charge distribution measurements was employed.

The apparatus to measure the conduction currents 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. A guard ring was installed at the measuring electrode side to avoid the effect of surface currents and to diminish the edge effect. The area of the measuring electrode was 6.02 cm<sup>2</sup>. Temperature control in the range of

30 to 100°C was carried out by placing the test cell in an air convection oven. A first measurement was made at 30°C and then the test temperature was raised to the next temperature without changing the test sample.

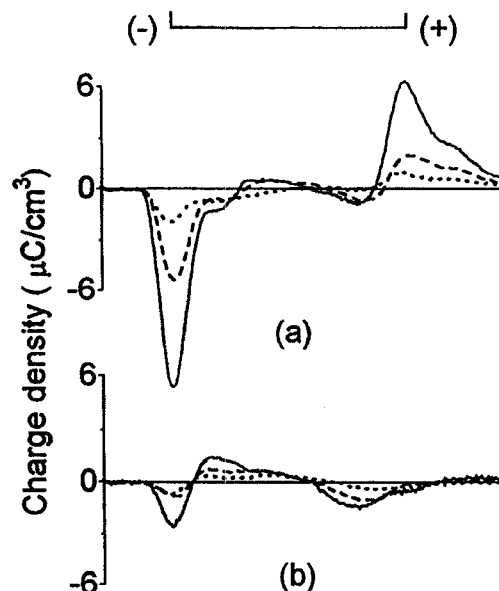


Figure 2. Charge distributions at various voltages of PE. (a) during charging at 6 (dot line), 10.8 (dashed line) and 21.6 kV (solid line), (b) after discharging.

## 3. EXPERIMENTAL RESULTS

### 3.1. CHARGE DISTRIBUTIONS IN PE

Typical charge distributions in PE at 6, 10.8 and 21.6 kV are shown in Figure 2. In this Figure, (a) shows the charge distribution obtained while the voltage was being applied (charging) and (b) that after voltage removal (discharging).

In PE, as shown in Figure 2(a), negative charge at the cathode and positive charge at the anode was found during charging. The amounts increased as the voltage increased. After the sample was short circuited, as shown in Figure 2(b), most charge induced at each electrode disappeared. Heterocharge, *i.e.* positive charge near the cathode and negative charge near the anode, was now found in the sample.

Figure 2(b) does not have the charge peak at the anode, which suggests that the electroacoustic signal generated at the anode has been attenuated while traveling through the sample to the detector. Therefore, the charge peak near the cathode is more meaningful than the one near the anode, which holds true in all charge distributions in this paper. A calibration has to be made in the future to obtain correct charge distributions.

The PE may contain impurities or ions which can contribute to the formation of heterocharge. The PE may possess polar groups in its chain ends because initiators such as oxygen or peroxide are used for the polymerization process. These polar groups may also contribute to the formation of heterocharge in PE [8].

The polarity change of accumulated charge near the cathode during charging and after discharging is due to a large induced charge at

the cathode. It can be hypothesized that the positive charge accumulated near the cathode, but the induced negative charge was so large that the positive charge peak was obscured. This negative-looking peak returned to the positive side after the large induced charge peak disappeared upon removing the voltage.

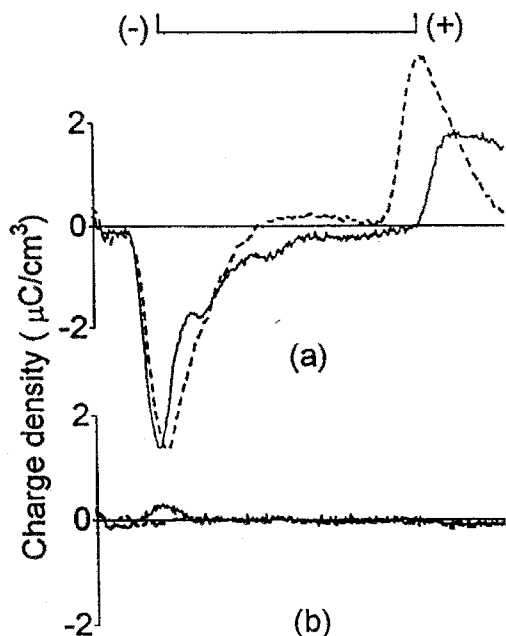


Figure 3. Charge distributions in ionomers: (a) during charging at 21.6 kV, (b) after discharging; Surlyn 1601 (solid line), Surlyn 1652 (dashed line).

### 3.2. CHARGE DISTRIBUTION IN IONOMERS

Charge distributions in two ionomers, Surlyn 1652 and Surlyn 1601, are shown in Figure 3, where (a) shows the charge distributions obtained during charging at 21.6 kV and (b) that remaining after discharging.

Almost no charge remained after discharging in both ionomers, which is quite different from PE. This difference may originate from the concentration of methacrylic acid (MAA) and carboxyl groups. The carboxyl group may act as a hopping site so that the charge injected during the charging step disappears easily to the electrodes upon removing the voltage. No such hopping sites exist in PE, so that the charge once formed within the sample may not disappear after discharging.

### 3.3. X-RAY ANALYSIS OF IONOMERS

Since the acid functions in ionomers are not fully neutralized (Table 1), it is questionable whether or not the ionomers used in this study contain ionic clusters. Therefore, X-ray diffraction patterns were obtained for PE, Surlyn 1652 and Surlyn 1601, the results of which are shown in Figure 4. The general shapes of the X-ray diffraction pattern of the ionomers are the same as for PE, which can be confirmed by the presence of a (110) peak at  $21.5^\circ$  and a (200) peak at  $23.0^\circ$  overlapped over a broad background representing the amorphous phase

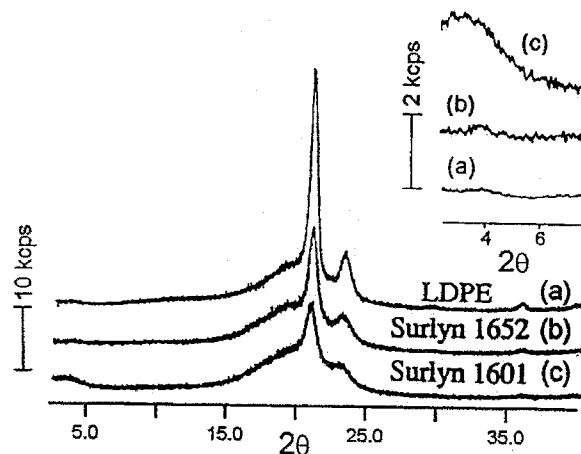


Figure 4. X-ray diffraction patterns of PE, Surlyn 1652 and Surlyn 1601.

[9]. In the low angle region, however, only Surlyn 1601 has a small peak at around  $3.7^\circ$  corresponding to a periodicity of  $\sim 30$  nm. This peak is known to be a characteristic peak for the ionic clusters [10–13]. The absence of ionic clusters in Surlyn 1652 may suggest that 18% of neutralization is not enough for forming the ionic clusters.

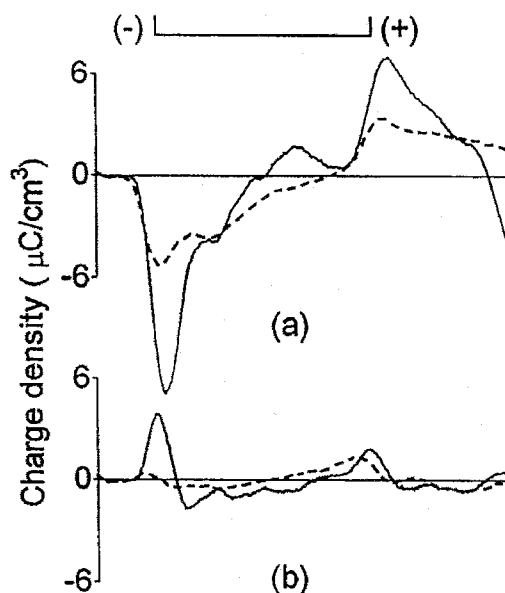


Figure 5. Charge distributions in PE/ionomer blends (90/10%wt): (a) during charging at 21.6 kV, (b) after discharging; PE/Surlyn 1601 blend (solid line), PE/Surlyn 1652 blend (dashed line).

### 3.4. CHARGE DISTRIBUTIONS IN PE/IONOMER BLENDS

Charge distributions in PE/ionomer blends (90/10%wt) are shown in Figure 5, where (a) shows the charge distribution obtained during charging at 21.6 kV and (b) that after discharging. In PE/Surlyn 1652 blend (Figure 5(a)), negative charge was found across the specimen with no positive charge near the anode. In the PE/Surlyn 1601 blend, on the other hand, negative charge was found near the cathode and positive charge in the bulk. It seems that the PE/Surlyn 1652 blend has more negative charge near the cathode. When the sample was short circuited (Figure 5(b)), the situation changed. In the PE/Surlyn

1652 blend, the negative charge peak was found in the first half of the specimen and the positive charge peak in the second half of the specimen. In the PE/Surlyn 1601 blend, however, negative charge was widely spread out and only small amount of positive charge was seen near the anode.

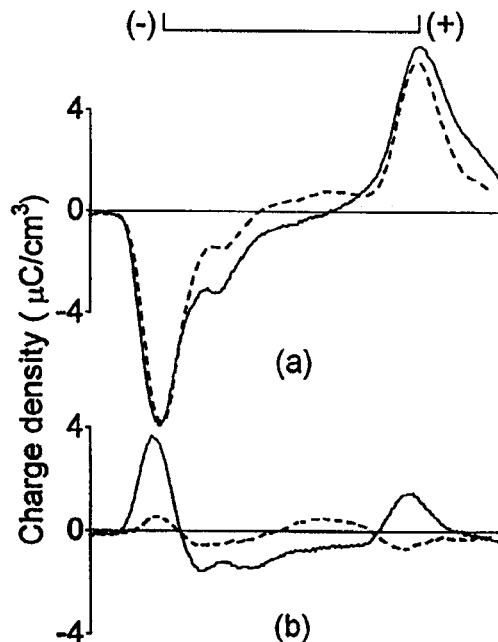


Figure 6. Charge distributions in PE/ionomer blends (50/50%wt): (a) during charging at 21.6 kV, (b) after discharging; PE/Surlyn 1601 blend (solid line), PE/Surlyn 1652 blend (dashed line).

Charge distributions in PE/ionomer blends (50/50%wt) are shown in Figure 6. In the PE/Surlyn 1652 blend, a homocharge formation was observed both during charging at 21.6 kV (Figure 6(a)) and after discharging (Figure 6(b)). It is of interest to note that the charge distribution after discharging was somewhat symmetrical in the sense that the first half contained negative charge and the second half positive charge. In the PE/Surlyn 1601 blend, on the other hand, negative charge accumulated across the specimen, and seemed to become larger after discharging, as shown in Figure 6(b). This feature is also quite different from the behavior in the PE/Surlyn 1652 blend.

### 3.5. CONDUCTION CURRENTS IN PE/IONOMER BLENDS

Current density  $J$  and electric field  $E$  curves of PE are shown in Figure 7. It can be found that the current density is proportional to the  $n$ th power of electric field, i.e.  $J = E^n$ . The power  $n \sim 1.0$  in the low field region and  $n \sim 2.0$  in the high field region, which may indicate a space-charge-limited conduction (SCLC) mechanism [14, 15].

$J$ - $E$  curves for two PE/ionomer blends are shown in Figure 8. Both samples show an increase of current density with an increase of electric field. At electric fields higher than  $10^7$  V/m, the PE shows current densities higher than the PE/ionomer blends. At  $3 \times 10^7$  V/m, for example, current densities of PE, PE/Surlyn 1601 (90/10%wt) and PE/Surlyn 1652 (90/10%wt) are  $1.44 \times 10^{-4}$  A/m<sup>2</sup>,  $6.50 \times 10^{-5}$  A/m<sup>2</sup>

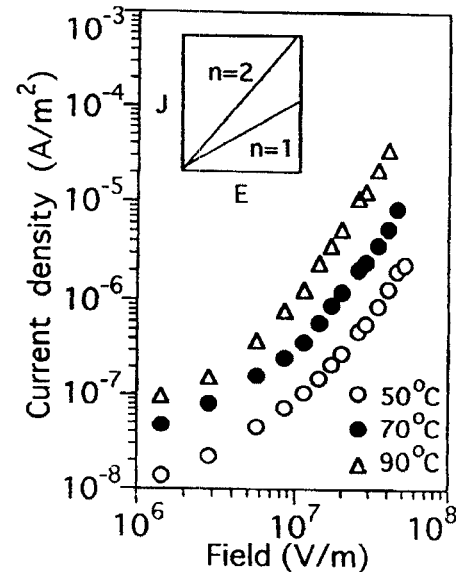


Figure 7.  $J$ - $E$  curves in PE.

Table 2. Intersection fields (MV/m).

Temp. °C	Ionomer, %wt		
	7	10	15
70	2	4	5.5
90	1	3	5

and  $6.77 \times 10^{-5}$  A/m<sup>2</sup>, respectively. It is also found that current density in PE/Surlyn 1601 blends are higher at lower electric fields and lower at higher electric fields than PE/Surlyn 1652 blends. The intersection fields become higher as both temperature and ionomer content increase (Table 2). Figure 9 shows the  $J$ - $E$  curves as parameterized by the Surlyn 1601 content in PE/Surlyn 1601 blends. One can see in this Figure that the current density at high fields becomes smaller as more Surlyn 1601 is added.

A change in  $dJ/dE$  at high fields was found in both PE/ionomer blends (Figures 7 and 8), the extent of which seems to become more as the Surlyn 1601 content increases (Figure 9). This change in  $dJ/dE$  has been reported with PE and other polymers [15-18]. Various mechanisms such as morphological changes caused by high field, heterocharge injection, bipolar injection and change of hopping distance have been proposed to explain the change in  $dJ/dE$  in polymers. In the present case, the result in Figure 9 suggests Surlyn 1601 present in the PE should be the major cause for the change of  $dJ/dE$ .

It is important in the present case to know whether or not the conduction mechanisms change at high fields. Literature information indicates that conduction mechanisms do not change in PE, crosslinked PE (XLPE) and PE/EVA blends, although there are some changes in  $dJ/dE$  [15, 19]. Therefore, we could expect no change in the conduction mechanisms in the present samples, although the slopes of the  $\log J$ - $\log E$  plots in PE/ionomer blends change from 2 to 1. Further work is needed to confirm this.

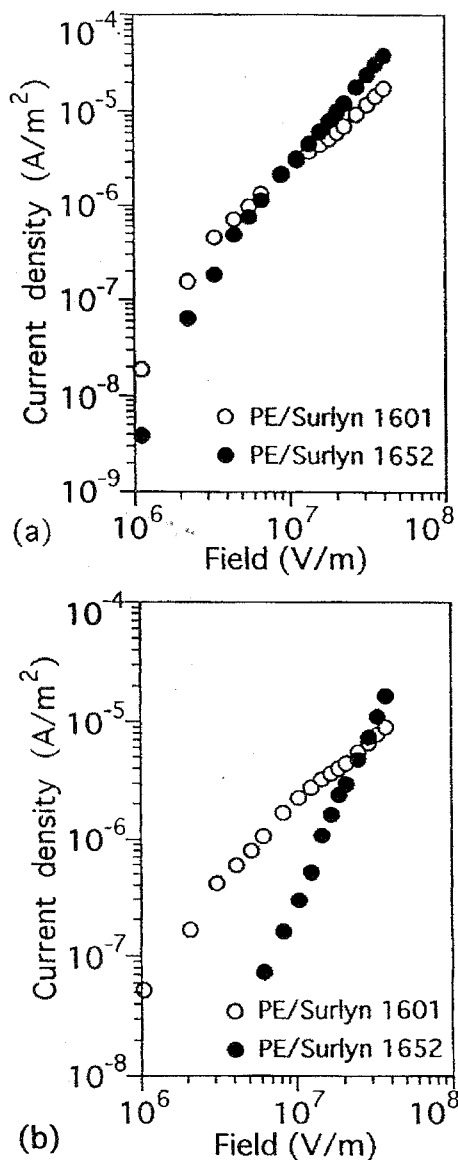


Figure 8.  $J$ - $E$  curves in PE/ionomer blends at 90°C: (a) Ionomer content: 7%wt, (b) 10%wt.

### 3.6. COMPARISON OF RESULTS WITH OTHERS

Earlier work carried out with a similar blend system claimed that the injected space charge is neutralized by the charge remaining inside the sample [1]. A study on the space charge phenomena using a thermal pulse method showed a relatively uniform distribution of negative charge when ionomers and PE were charged at high temperature, typically at 60°C for 5 h [20]. Interestingly, XLPE also showed a uniform distribution of negative space charge, contrary to those reported by others [7, 21]. In the present study, on the other hand, Surllyn 1652 showed negative charge near the cathode and positive charge near the anode while Surllyn 1601 showed a relatively uniform distribution of negative charge.

These differences could originate mainly from different experimental conditions and samples. High temperatures will facilitate both

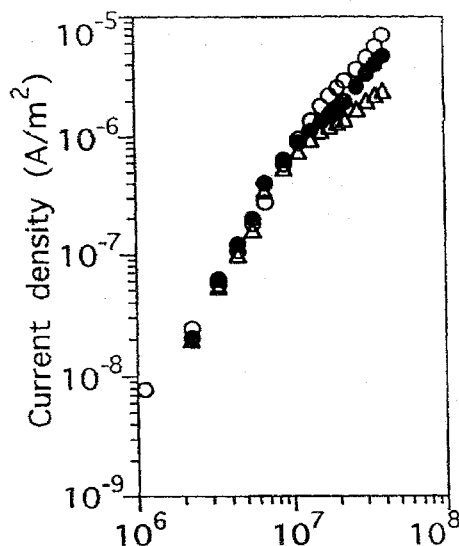


Figure 9.  $J$ - $E$  curves in PE/ionomer blends at 70°C: Surllyn 1601 content: 3%wt (○), 7%wt (●), 10%wt (△).

chain motion and charge migration. In this situation, space charge is expected to increase and its distribution to become uniform. High charging voltages will also enhance charge injection. The present samples are expected to show similar features if charged at high temperature for a long time. Moreover, different samples should produce different charge distributions.

In the present study, charging the samples at high temperatures was not adopted because of two reasons. One is the instrumental limitation. The instrument to measure charge distributions uses PVDF film as a piezoelectric transducer. This polymer cannot be used at high temperature because it loses its piezoelectricity at high temperatures. The other reason is that if the samples are charged at sufficiently high temperatures, a major difference between the two blends will be the magnitude of charge. However, what we need to know in the present study is how these blends behave during the charging and discharging processes.

### 3.7. COMPARISON BETWEEN TWO IONOMER BLENDS

The present results suggest that there are some components which prohibit charge transport in ionomers and blends, especially in Surllyn 1601. The component in Surllyn 1601 must have a strong affinity for electrons, which is stronger in Surllyn 1601 than in Surllyn 1652.

The differences in charge behavior between two PE/ionomer blends should originate from the differences in their chemical natures. The ionomer is an ethylene methacrylic acid (EMA) copolymer, the acid function of which is neutralized with metal ions such as  $Zn^{2+}$  (Surllyn 1652) or  $Na^+$  (Surllyn 1601). These two ionomers are chemically different in such parameters as concentration of methacrylic acid (MAA), extent of neutralization and ion type, as shown in Table 1.

Chemically, one MAA has one carboxyl group, so that the difference in the concentration of MAA indicates the difference in the concentration of carboxyl group. Since the acid function was partially

neutralized with metal cations, *i.e.* 18% for Surlyn 1652 and 53% for Surlyn 1601, all metal cations could be consumed to form the salts and thereafter are not free to move. However, Surlyn 1601 possesses ionic clusters while Surlyn 1652 does not, as shown in Figure 4, due to the differences in the extent of neutralization. 18% of neutralization is not sufficient to form ionic clusters in the case of Surlyn 1652.

Of these, whether or not the ionomer possesses ionic clusters may be the major cause for the differences in charge behavior in these blends. The ionic clusters are the aggregation of ionic pairs. Ionic clusters should trap electrons injected from the electrodes very effectively, because they have strong affinity for electrons. They will not allow the trapped electrons to dissipate easily during the discharging process, with the net result being a uniform distribution of negative charge after discharging. For the same reason, conduction currents decrease as Surlyn 1601 content increases.

The uniform distribution of charge in the case of Surlyn 1601 can be attributed to the combined effects of carboxyl groups and ionic clusters. Carbonyls in the carboxyl groups can act as hopping sites for charge transport, so that the charge can penetrate easily into the bulk of sample. These charges should be trapped at the trapping sites associated with ionic clusters. However, since there are no ionic clusters in Surlyn 1652, the charge will dissipate easily upon discharging, the net result being an accumulation of a small amount of homocharge.

In conclusion, a decrease of TSC at high poling fields in PE/Surlyn 1601 blends resulted from the evening out of the charge distribution, although there is a large amount of negative charge in the sample.

#### 4. CONCLUSIONS

**H**ETEROCHARGE accumulated in PE during the voltage application but homocharge appeared in ionomers. When the sample was short circuited, a considerable amount of heterocharge remained in the PE but no charge remained in either ionomer. This may be due to the carboxyl group acting as a hopping site.

PE shows higher current densities at high fields than either PE/ionomer blend. The current density in PE/Surlyn 1652 blends is higher at low fields and becomes lower at high fields compared with PE/Surlyn 1652 blends.

Most charge injected into the PE/Surlyn 1652 blends during the charging step disappeared to each electrode upon discharging, whereas a considerable amount of injected charge migrated inside the specimen upon discharging the PE/Surlyn 1601 blends. This migration results in a uniform distribution of negative charge. This was attributed to the ionic clusters in Surlyn 1601 having a strong electron affinity. This work was initiated to elucidate the reasons why the TSC of PE/Surlyn 1601 blend decreased at HV while that of PE/Surlyn 1652 blend increased with the increase of voltage. We conclude that a smaller TSC in PE/Surlyn 1601 blends at high poling fields results from an evening out of the charge distribution due to the ionic clusters in the Surlyn 1601.

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