

Space Charge Distributions in EPDM Compounds

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ABSTRACT

The formation of space charge in EPDM (ethylene-propylene-diene terpolymer) filled with ATH (alumina trihydrate) or clay has been investigated by measuring charge distributions. It is found that the type and amount of space charge developed in crosslinked EPDM or its compounds is governed by the type of diene in EPDM and the composition of the semicon electrodes. The amount of charge in the EPDM compounds containing 1,4-hexadiene decreases with an increase of ATH content and increases with an increase of clay content. The heat treatment of EPDM compounds in a vacuum oven increases the amount of space charge in them. These features were explained by the effects of low molecular weight molecules present at the surface of fillers. It is found that the homocharge increases as the clay content increases, while EVA decreases the homocharge in the EPDM compounds. Possible reasons for these results are discussed.

1. INTRODUCTION

POLYMER/FILLER composites are frequently used in the insulation of electrical equipment. Typical examples are insulating materials for EPR (ethylene propylene rubber) cables and cable joints made of a mixture of EPDM (ethylene-propylene-diene terpolymer) and some fillers such as alumina trihydrate ATH (alumina trihydrate), alumina (Al_2O_3), silica (SiO_2) and clay. These fillers are added to the EPDM to impart improved mechanical properties, flame retardancy or tracking resistance.

In the case of cable splices, the interfaces between the cable insulation layer of XLPE (crosslinked polyethylene) and the EPDM insulation of splices provide weak spots. An example of interfacial phenomena is charge accumulation at the interfaces caused by a structural discontinuity. Of these, charge formation in DCP (dicumyl peroxide) cured polyethylene, *i.e.* XLPE, is relatively well-documented [1, 2]. It is believed among engineers working in this field that volatile residues encourage the formation of heterocharge. However, charge formation in EPDM/filler compounds is not well known. In EPDM/filler compounds, a wide variety of compositions are possible, depending on the type and concentration of fillers, which renders prediction of the electrical properties very difficult.

Table 1. Specifications of EPDM samples used in this study [6].

EPDM	Diene type	Ethylene %wt	Propylene %wt	Diene %wt	Volatile %wt
EP-H	HD	Data not available			
EP-E1	ENB	51.4	45.5	2.49	0.60
EP-E2	ENB	51.6	43.1	4.65	0.63
EP-E3	ENB	52.2	38.9	8.28	0.65

The role of the interface between the filler and the polymer becomes important in polymer compounds. A general feature is that the fillers increase the charge due to interfacial polarization effects. For example, Yin *et al.* [3, 4] have reported that the charge increases when fillers such as kaolin and clay are added to LDPE (low density polyethylene). A similar result was observed by Jeffery and Damon [5] for a mixture composed of clay and EPR.

This work deals with space charge formation in EPDM /ATH compounds used as base materials for cable splices. The effects of heat treatment on the formation of space charge in these materials and the effects of different types of dienes and fillers were also investigated.

Table 2. Compositions of compound samples used in this study.

Compound	EPDM	ATH phr	Clay phr	DCP phr
XLEP-H/ATH Compounds	EP-H	30	-	2
	EP-H	50	-	2
	EP-H	70	-	2
	EP-H	100	-	2
	EP-H	150	-	2
	EP-H	200	-	2
XLEP-H/Clay Compounds	EP-H	-	50	2
	EP-H	-	100	2
	EP-H	-	150	2
	EP-H	-	200	2

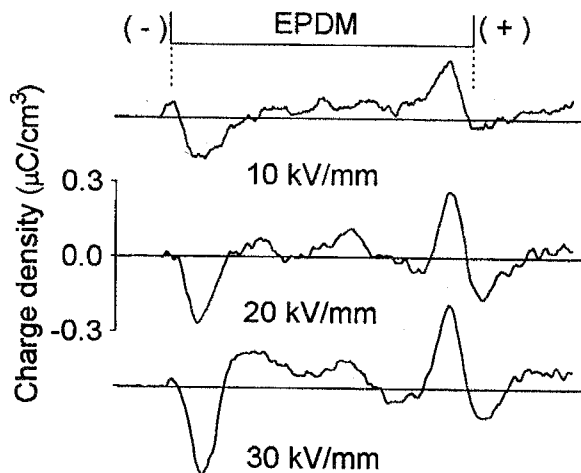


Figure 1. Charge distributions in an XLEP-H sample.

2. EXPERIMENTAL PROCEDURES

The EPDM/ATH compound used in this study was provided by a local splice manufacturer. This compound contains 70 parts per hundred (phr) resin of ATH, processing aids and DCP. EPDM/filler compounds containing different ATH and clay content up to 200 phr were prepared in the laboratory by kneading at 80°C for 10 min, followed by roll-milling for another 10 min. DCP was added during the roll-milling process in order to prevent premature decomposition during the kneading process.

Details of the EPDM and compound samples used in this study are summarized in Tables 1 and 2. Most experiments were carried out with the EPDM containing HD (1,4-hexadiene) as the diene. These samples were designated EP-H for uncrosslinked materials and XLEP-H for crosslinked materials. For the study of effects of different dienes, however, EPDM containing dienes such as ENB (5-ethylene-2-norbornene) were used as base polymers for the compounds. These EPDM were obtained from Kumho EP Co., Korea. These samples were designated EP-E samples, for example EP-E1 for 2.49% wt, EP-E2 for 4.65% wt and EP-E3 for 8.28% wt. The corresponding crosslinked materials were designated XLEP-E1, XLEP-E2 and XLEP-E3. The crosslinking reaction was carried out at 170°C for 10 min using a hot press. Cured samples were heat treated in a vacuum oven when needed. Typical conditions for heat treatment were either 80 or 100°C for duration \leq 200 h.

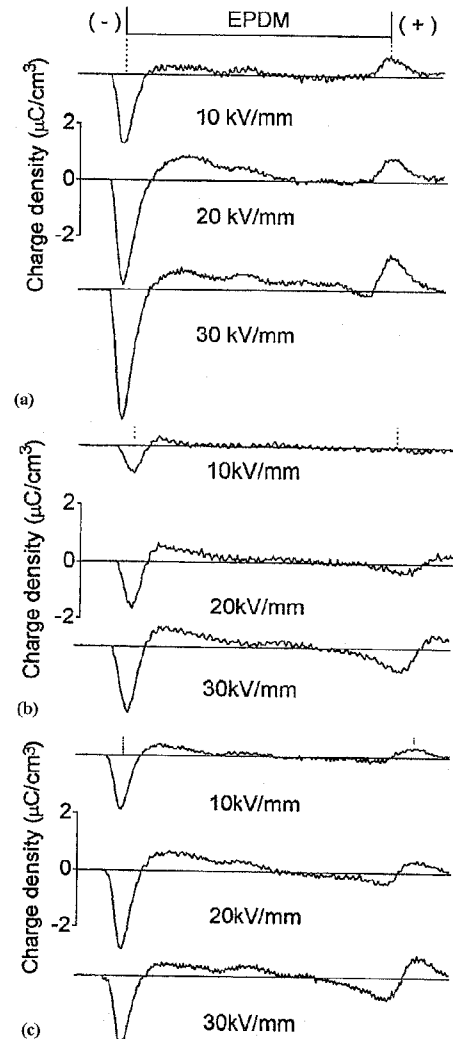


Figure 2. Charge distributions in XLEP-E samples: (a) XLEP-E1, (b) XLEP-E2 and (c) XLEP-E3.

Charge distributions were measured by a PEA method, details of which have been described elsewhere [2, 7]. An electric pulse with an amplitude of 2 kV and a width of 10 ns was used. Most charge distributions were obtained using EPDM-based semicon electrodes.

EVA (ethylene-vinyl-acetate) based semicon electrodes were also used for the comparison of effects of type of semicon electrodes. The latter were used extensively to enhance the adhesion between XLPE and EPDM samples and to simulate the situation encountered with cable splices. These electrodes were prepared by compression molding at 170°C for 10 min. To eliminate the effects of volatile residues in DCP-crosslinked semiconductive electrodes, they were vacuum degassed at 80°C for 100 h before being used as electrodes [1, 2]. The typical thickness of the EPDM/ATH compound samples was 0.7 mm and of the semicon electrodes was 0.2 mm. Measurements of charge distributions typically were made within 2 min after short-circuiting at the end of the application of voltage for 30 min. Therefore, most examples of charge distributions given in this paper are the distributions of charge remaining in the sample after the discharge. Since the spatial resolution of the PEA system was 45 μ m, small peaks in measured charge distributions

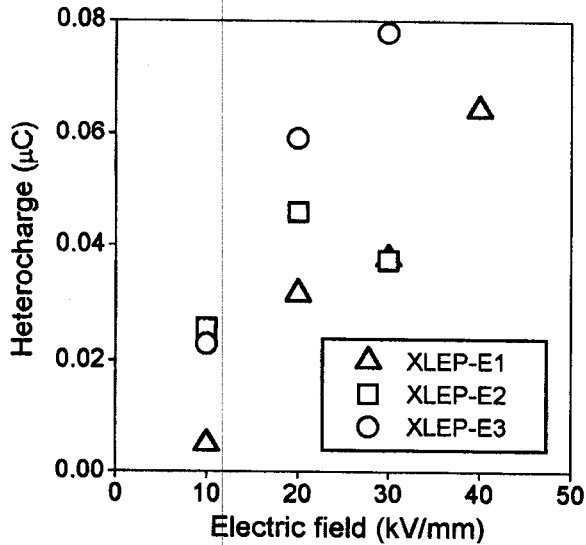


Figure 3. Heterocharge near the cathode vs. applied field in XLEP-E samples.

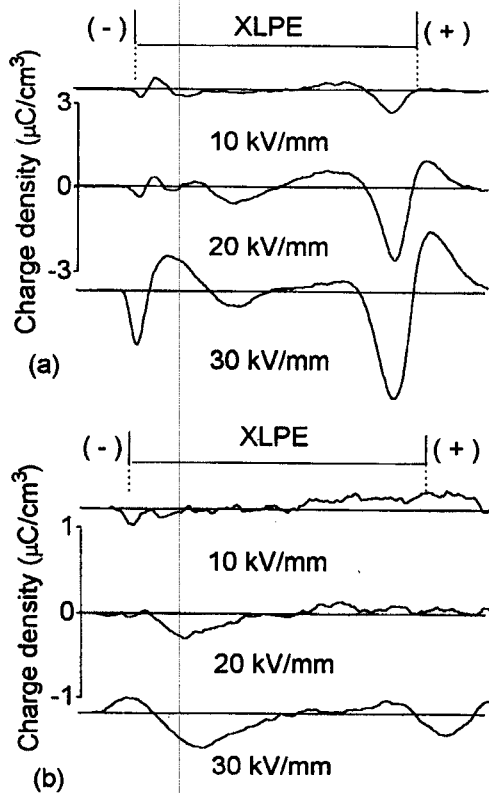


Figure 4. Effects of types of semicon electrodes on the charge distributions of DCP-cured XLPE: (a) EVA-based semicon electrode, (b) EPDM-based semicon electrode.

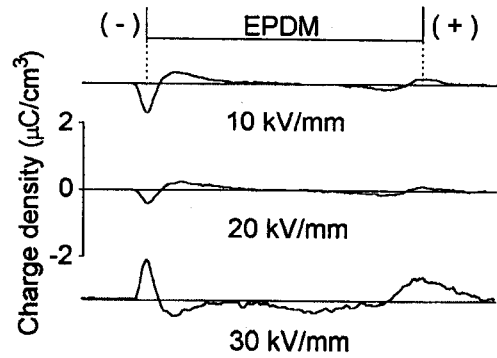


Figure 5. Charge distributions in XLEP-H compound (ATH 70 phr).

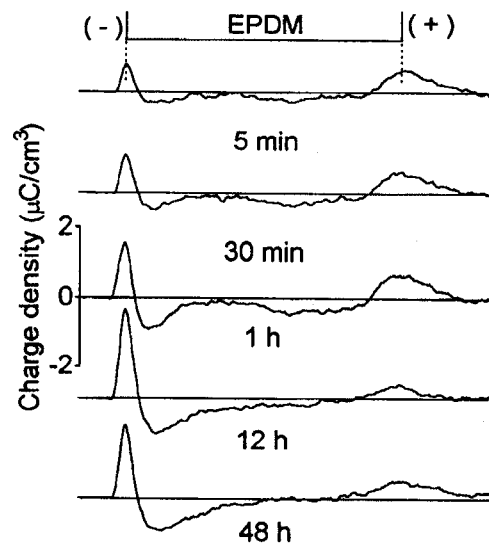


Figure 6. Evolution of charge distributions in XLEP-H compound (ATH 70 phr) as a function of time of field application at 30 kV/mm.

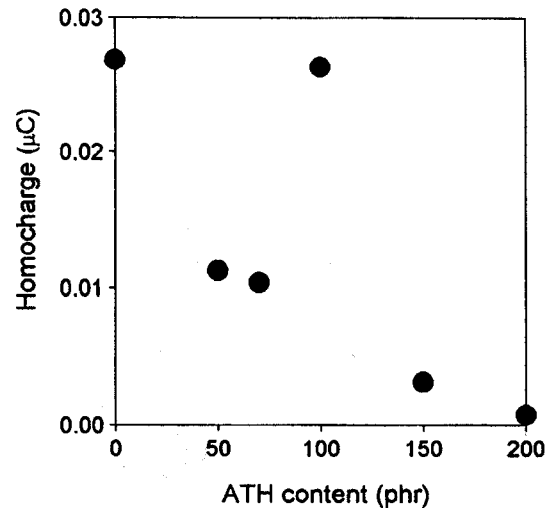


Figure 7. Charge at 30 kV/mm in XLEP-H compounds as a function of ATH content.

3. EXPERIMENTAL RESULTS

3.1. EPDM

Figures 1 and 2 show the charge distributions of crosslinked EPDM (XLEP) without any fillers. Homocharge develops in XLEP-H samples

whose widths are < 45 μm are not significant.

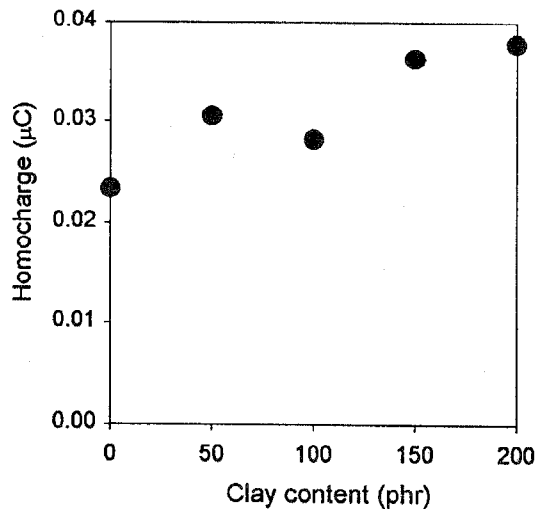


Figure 8. Charge at 30 kV/mm in XLEP-H compounds (clay) as a function of clay content.

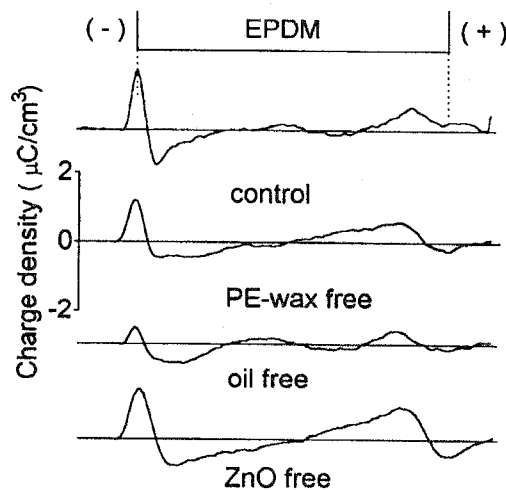


Figure 9. Effects of components of XLEP-H compound on the charge distributions (ATH: 30 phr) at 30 kV/mm.

while heterocharge develops in all XLEP-E samples, although they have been crosslinked under the same conditions using 1.0 phr of DCP. The observation of heterocharge in DCP-cured ENB-type EPDM agrees with the previous report by Kogure *et al.* [9]. They also found that the charge changes type from heterocharge in an as-cured condition to homocharge in a vacuum-evacuated condition. A plot of charge vs. applied field in Figure 3 shows increasing heterocharge with increasing applied field, although the XLEP-E3 sample shows a decrease of heterocharge at higher fields.

Figure 4 shows the effects of the type of semicon electrodes on the charge distributions in DCP-cured XLPE. Heterocharge is observed in the XLPE with EVA-based semicon electrodes, as found in other reports [1, 2]. In the case of XLPE with EPDM-based semicon electrodes, a very small amount of homocharge is distributed broadly in the sample. This result indicates that the type of semicon electrodes is one of the important factors in the determination of type of charge accumulation in DCP-cured XLPE. The importance of the composition of the semicon electrodes has been addressed earlier by many researchers [2, 8].

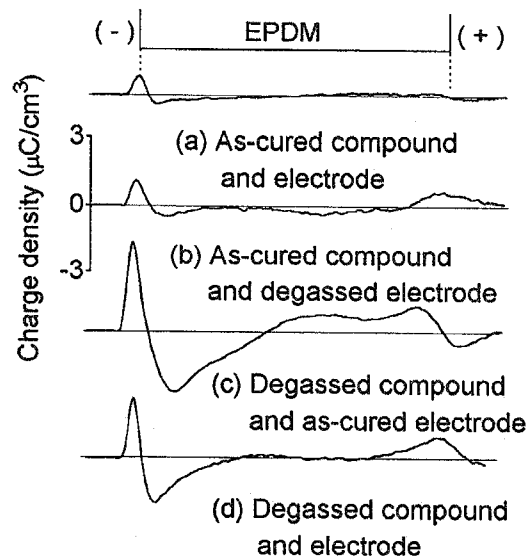


Figure 10. Effects of heat treatment conditions on the charge distributions at 30 kV/mm in XLEP-H compound (ATH 70 phr).

3.2. EPDM/ATH COMPOUNDS

Figure 5 shows the charge distributions in the XLEP-H/ATH compound containing 70 phr of ATH. Heterocharge is observed at 10 kV, which decreases with the increase of voltage, and homocharge is observed at 30 kV/mm. This data indicates that the ions or dipoles are polarized to form heterocharge right after the voltage application. This heterocharge increases the local electric field at the electrode/sample interface, which in turn stimulates the injection of homocharge from the electrodes. The net result is an apparent decrease of heterocharge with the increase of voltage and finally homocharge is observed at HV, 30 kV in this particular case. Figure 6 shows the evolution of charge distributions as a function of time of voltage application. As shown, homocharge develops from the beginning of the application of 30 kV/mm and keeps increasing as a function of time of field application.

Figure 7 shows the charge near the cathode in the XLEP-H/ATH compounds as a function of ATH content. The shapes of the charge distributions are the same in that all samples showed negative charge near the cathode, *i.e.* homocharge. As shown, the amount of charge near the cathode decreases with the increase of ATH content, although the EPDM containing 100 phr of ATH shows a relatively large homocharge.

A decrease of charge near the cathode as a function of ATH content does not agree with previous reports. For example, Yin *et al.* [3] reported that the charge measured by the TSC (thermally stimulated current) technique increased when fillers such as clay and zeolite were added to LDPE. Jeffery and Damon [5] also reported an increase of charge in clay-filled EPR with an increase of clay content to 50 phr. However, our results indicate that the addition of ATH to EP-H reduces the amount of space charge. In order to clarify this discrepancy, clay was added to the same EPDM and the charge distributions were measured. As shown in Figure 8, the amount of charge in the XLEP-H containing clay increases with the increase of clay content, which agrees well with the previous observation [5].

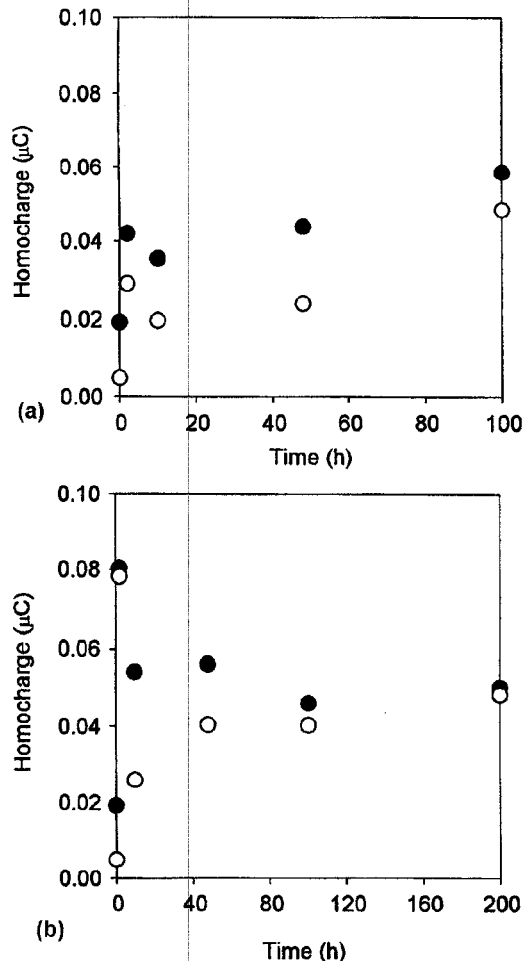


Figure 11. Charge near the cathode at 30 kV/mm in heat treated XLEP-H compound (ATH 70 phr): (a) 80°C, (b) 100°C. Fresh semicon electrode (closed circle), degassed semicon electrode (open circle).

Figure 9 shows the effects of components of the XLEP-H containing 30 phr of ATH on the charge distributions. As shown, all samples show only homocharge, which indicates that no components can change the type of charge in the XLEP-H containing ATH. However, the charge formation becomes confined to the electrode-sample interface as more components are added to the EPDM. This could indicate that injected charges are trapped at these components present near the electrodes, which prevents the injected charge from migrating into a deeper region of the sample.

3.3. EFFECTS OF HEAT TREATMENT

The effects of heat treatment on XLEP-H/ATH compounds and semicon electrodes are shown in Figure 10. The heat treatment was done at 80°C for 48 h in a vacuum oven. XLEP-H containing 70 phr of ATH was used in the measurements.

All samples show the accumulation of homocharge, and the charge densities depend on the sample conditions. As-pressed compound and semicon electrodes show homocharge (Figure 10(a)). This homocharge gets smaller when only semicon electrodes are heat treated in a vacuum oven (Figure 10(b)). The homocharge gets larger when only compound

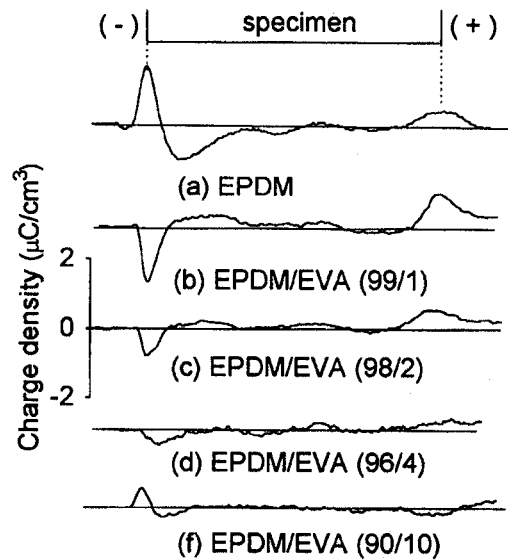


Figure 12. Charge distributions at 30 kV in XLEP-H/EVA/ATH compounds (ATH 100 phr).

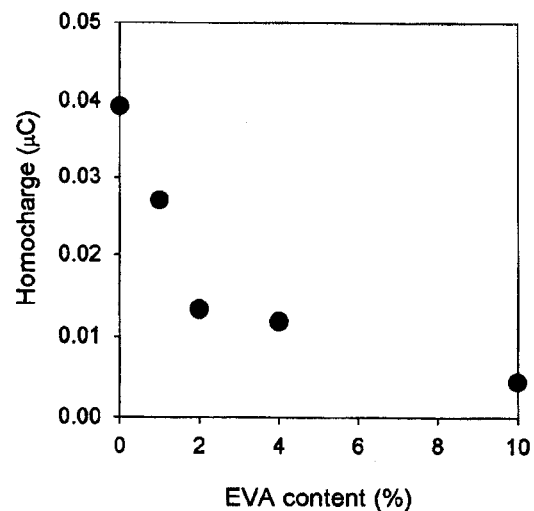


Figure 13. Charge near the cathode at 30 kV in XLEP-H/EVA/ATH compounds (ATH 100 phr).

is vacuum treated (Figure 10(c)). When both compound and semicon electrodes are treated, the homocharge gets slightly smaller again compared to the case where only compound is heat treated in a vacuum oven (Compare Figure 10(d) and 10(c)).

More extensive heat treatment was carried out at both 80 and 100°C to 200 h in a vacuum oven. The results are shown in Figure 11. When the compound is treated at 80°C for up to 100 h in a vacuum oven, a fast increase of homocharge during the first a few hours is observed, and then a gradual increase beyond this time. This feature becomes more prominent in 100°C treated samples in that the charge increases sharply during < 4 h and then saturates to a certain level. For both cases, the vacuum degassing of semicon electrodes reduces homocharge, as described in Figure 10.

3.4. EFFECTS OF EVA

In order to study the effects of EVA on the charge formation in XLEP-H compounds, EP-H/EVA blends were used as the base material for XLEP-H/ATH compounds. The ATH content is 100 phr and the compositions of these compounds was changed a little to produce a larger charge. Figure 12 shows the charge distributions in these compounds and Figure 13 shows the charge near the cathode. As shown, the charge near the cathode decreases considerably when a small amount of EVA is added to the EP-H.

The carbonyl groups in EVA can act as charge trapping and hopping sites depending on their concentration, or equivalently their average separation [10–12]. The fact that the charge decreases with the increase of EVA content indicates that these carbonyl groups acted as charge hopping sites. The charge injected during the voltage application dissipates easily upon discharging through these carbonyl groups, with the net result being a decrease of homocharge.

4. DISCUSSION AND SUMMARY

It is found that homocharge develops in DCP-cured XLEP-H and its compounds while heterocharge develops in DCP-cured XLEP-E samples. Kogure *et al.* [9] found with DCP-cured XLEP-E samples that a vacuum degassing decreases heterocharge and finally homocharge develops, as is the case for DCP-cured XLPE [1, 2]. Therefore, it can be said that heterocharge in DCP-cured XLEP-E samples is due to volatile residues such as acetophenone and cumyl alcohol formed by the thermal decomposition of DCP. These residues should be the same for both EPDM and PE. The role of volatile residues is then expected to impose similar effects to both EPDM and XLPE. Since volatile residues lead to increased heterocharge, XLEP-H samples are also expected to show heterocharge. However, the observation is that XLEP-H and its compounds show homocharge. The only difference between XLEP-H and XLEP-E samples is the type of diene, *i.e.* HD for XLEP-H and ENB for XLEP-E. Therefore, it can be said that the HD in XLEP-H samples promote the injection or trapping of charge, which overwhelms the tendency of volatile residues to encourage the formation of heterocharge. All these facts suggest that the type of diene in EPDM plays an important role in determining the type of charge in XLEP samples.

With the semicon electrodes fixed, the type and amount of space charge in EPDM or its compounds are determined by the competition between the effects of dienes and of volatile residues. Heterocharge is observed when the effect of the volatile residues dominates, which is the case for XLEP-E samples. On the other hand, homocharge is observed when the effect of dienes dominates, which is the case for an XLEP-H sample and its compounds. For both cases, the composition of the semicon electrodes, for example the type of base polymer, plays an important role in determining the type of space charge in EPDM and its compounds. EPDM-based semicon electrodes suppress heterocharge formation considerably, compared to EVA-based semicon electrodes.

Homocharge is observed in all XLEP-H compounds with ATH and clay. However, this homocharge in XLEP-H/ATH compounds decreases with the increase of ATH content, whereas it increases with the increase of clay content. The increase due to clay could be explained by the enhancement of interfacial polarization, *i.e.* enhanced trapping of injected

charge, at the interfaces between EPDM and clay. In the ATH-filled XLEP-H, the total amount of EPDM-ATH interfaces should increase with the increase of ATH content. If the trapping of charge at the polymer-filler interfaces is a major mechanism for charge formation, the amount of homocharge should increase as a function of ATH content. However, the opposite is observed in the ATH-filled XLEP-H samples. The decrease of homocharge with the increase of ATH content could be attributed to the nature of the surface of ATH fillers. Two cases are possible. One possibility is related to water molecules or ionic impurities at the surface of fillers. In ATH, the alumina molecules are coordinated with H₂O molecules. We surmise that the water molecules in the ATH provide dipoles which can develop a heterocharge. The heterocharge offsets the homocharge formed at the XLEP-H/ATH interfaces. It seems that the contribution of water molecules in the ATH is larger than those of the XLEP-H/ATH interfaces. Dipoles form also by the polarization of ionic impurities at the surface of ATH fillers [3]. The other possibility is that the water molecules or hydroxyl groups at the surface of the ATH filler can provide a bridge for charge transport. Through this bridge, the charge injected from the electrodes during the voltage application dissipates easily upon discharging, with the net result being a decrease of homocharge at higher ATH content.

The heat treatment of XLEP-H compounds containing ATH in a vacuum oven increases homocharge in the compounds containing ATH. Two phenomena can take place on heat treating XLEP-H/ATH compounds in a vacuum oven: one is isothermal crystallization and the other is a change in the nature of the XLEP-H/ATH interfaces. Isothermal crystallization creates microscopic interfaces at the boundaries of crystalline and amorphous phases where the charge can accumulate. However, DSC (differential scanning calorimeter) thermograms with the heat treated samples did not show any evidence of an endothermic peak around the heat treatment temperatures. This implies that there was no isothermal crystallization upon treating the compounds at either 80 or 100°C, for < 200 h. Therefore, the first possibility that the trapping of charge occurring at the crystalline-amorphous interfaces can be excluded. With regard to the second possibility, it is very difficult to know what type of change might have occurred at the EPDM/ATH interfaces on heat treatment. It could be that the moisture or the hydroxyl groups at the surface of ATH fillers could act as hopping sites for charge transport, providing the bridge for charge to migrate. When moisture exists at the filler surface, the homocharge injected during the voltage application would dissipate easily. However, if the moisture is removed by a vacuum treatment, the charge cannot dissipate readily when the sample is short circuited. The net result would be an increase of homocharge.

In summary, the type of diene and the composition of the semicon electrodes were found to be the most important factors in the determination of the type and amount of space charge in DCP-cured EP-H and its compounds containing ATH fillers. Heat treatment of XLEP-H compounds containing ATH increases the homocharge. This homocharge decreases with an increase of ATH content. All these observations were explained by effects due to the nature of the surface of ATH. It was also found that clay increases the homocharge in clay-filled XLEP-H compounds. Homocharge in the XLEP-H/clay compounds decreases considerably when a small amount of EVA is blended with the EP-H.

ACKNOWLEDGMENT

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