

Interfacial Charge in Polyethylene/Ethylene Vinylacetate Laminates

Kwang S. Suh, Jae Y. Kim, Hong S. Noh
and Chang R. Lee

Department of Materials Science, Korea University, Seoul, Korea

ABSTRACT

Space charge formation in polyethylene (PE)/ethylene vinylacetate copolymer (EVA) laminates has been investigated using a pulsed electroacoustic method. The PE shows heterocharge while the EVA shows a broad distribution of positive charge over the sample. The positive charge in EVA decreases with the increase of vinylacetate (VA) content in EVA. Interfacial charge is found in all laminates and remains unchanged by heat treatment at 100°C to 1 h and by coating chemicals such as silicone oil and trimethylolpropane trimethacrylate at the interfaces. This interfacial charge distorts the electric field distribution in the direction of increasing the electric field in the PE layers. The charge distribution in PE/EVA blends has been measured and is explained via the results obtained with the laminates.

1. INTRODUCTION

BEING widely used for electrical insulation, polyethylene (PE) suffers from drawbacks such as treeing and space charge phenomena. These problems may be overcome by blending the proper polymers. For example, ethylene vinylacetate copolymer (EVA) may be used for retarding tree propagation in PE and ionomers may be used for improving the breakdown strength and diminishing the space charge accumulation in PE [1-5].

When the polymers are blended, the interfaces between phases become important in the electrical performance of systems insulated by such heterogeneous materials. A recent approach in the study of interfacial phenomena in polymer blends is to utilize laminated samples. Suzuoki *et al.* [6] reported thermally stimulated current results for PE/EVA laminates. They found that the charge develops at the interfaces and a positive charge (holes) injected from the EVA side accumulates near the interface. Hozumi *et al.* [7] also found an accumulation of space charge at the interfaces of PE/EVA laminates. It is generally accepted that interfacial charges are observed in all laminate samples [8, 9].

The authors have also worked with PE/EVA laminates and found that space charge accumulates at the interfaces, resulting in a distortion of the electric field distribution [10]. However, this work has been confined to EVA with a vinylacetate (VA) content in the range of 10 to 15%. The EVA is a copolymer of ethylene and VA units in which these two units are incorporated randomly.

Since the VA unit has a polar carbonyl group which has an average effective dipole moment of 1.8 D [11], the electrical properties of EVA should vary depending on the VA content. The space charge behavior in PE/EVA laminates is then expected to change also. In addition, it is of interest to see how the interfacial charge changes due to modification of the interfacial conditions.

This work, a continuation of our previous work [10] on the space charge in PE/EVA laminates and blends, contains experimental results for the laminates of PE and EVA with VA contents of 5.2, 15, and 28%. The effects of modification of interfaces using heat treatment and chemical coating on the interfacial charge also were investigated. The results for the laminates were compared with those of PE/EVA blends.

2. EXPERIMENTAL PROCEDURES

The parent polymers used in this study are PE and EVA. The density and melt index of the PE (HY 830, Hanwha Chemical Co., Korea) are 0.920 g/cm³ and 2.0 g/10 min, respectively. The nominal weight percentages of VA in EVA were 5.2, 15, and 28%. These samples were designated as EVA 5 (EVA 2030, Hanwha Chemical Co., Korea), EVA 15 (EVA 1315, Hanwha Chemical Co., Korea) and EVA 28 (EVAFLEX 260, Mitsui-DuPont, Japan), respectively.

An overall method to prepare the samples, measure the charge distributions and calculate the electric field distributions from the measured charge distribution data has been described in our previous report [10]. In addition, the modification of the interface of

the laminates was made by coating with chemicals such as silicone oil and trimethylolpropane trimethacrylate (crosslinking coagent; CA) and treating in an air convection oven at 100°C for 1 h. The chemical was coated onto the surface of the EVA. This crosslinking coagent was used because it was effective in reducing the charge at the interfaces of PE laminates [12].

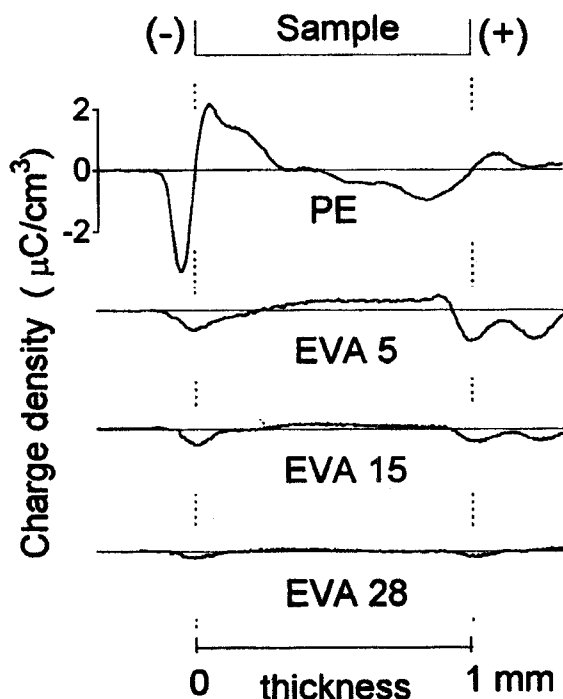


Figure 1. Charge distributions of PE and EVA immediately after short circuiting (40 kV).

3. EXPERIMENTAL RESULTS

3.1. PARENT POLYMERS

Figure 1 shows charge distributions at 40 kV in PE and EVA. These charge distributions were measured immediately after the sample was short circuited, so they are the residual charges remaining immediately after the discharge.

Polyethylene shows a heterocharge, *i.e.* positive charge near the cathode and negative charge near the anode, which may originate from impurities, polar groups and/or low molecular weight short PE chains [13]. The EVA shows a broad distribution of positive charge over the sample. This observation agrees with the previous observation by Suzuoki *et al.* [6]. The magnitude of positive charge in EVA decreases with the increase of VA content in the EVA. The EVA contains carbonyl groups which can act as hopping sites for charge transport [14, 15], although the carbonyls can act as trapping sites [16, 17]. The number of hopping sites should increase with the increase of VA content in EVA, resulting in a decrease of residual charge in EVA after the sample is short circuited.

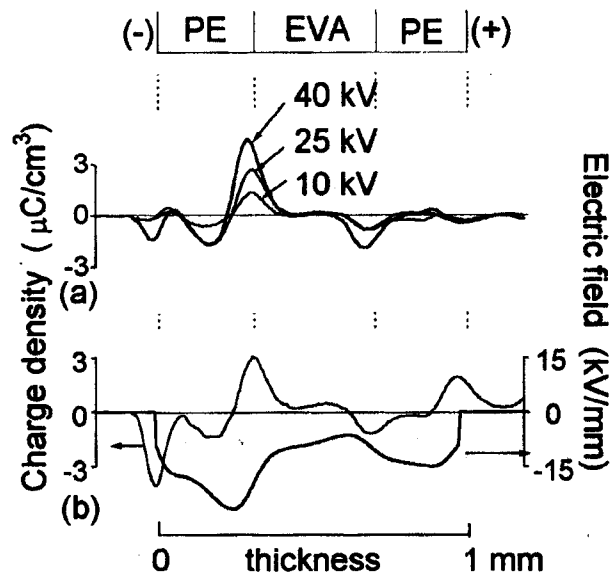


Figure 2. Charge distributions in PE/EVA 15/PE laminates: (a) charge distributions immediately after short circuiting, (b) charge and electric field distributions at 20 kV during the voltage application [10].

3.2. PE/EVA 15 LAMINATES

Figure 2 shows the spatial charge and electric field distribution of triple layer laminates, PE/EVA 15/PE laminates [10]. In these Figures, (a) shows the charge distribution at 10, 25 and 40 kV after short circuiting and (b) shows the charge and electric field distributions at 20 kV during the voltage application.

In PE/EVA 15/PE laminates, negative charge is found in the PE layer at the cathode side. The charge distribution in the PE layer at the anode side is not clear because the signal generated in this region is attenuated considerably while traveling to the piezoelectric detector. A large positive interfacial charge peak is found at the PE/EVA 15 interface at the cathode side while a negative interfacial charge peak is found at the EVA 15/PE interface at the anode side. Almost no charge develops in the EVA layer. It is seen that the electric field in the PE layer is much higher than in the EVA layer. At an average field of 18 kV/mm, for example, the electric field of the PE layer reaches 24 kV/mm in the PE/EVA/PE laminate. Similar features, except for the polarity of interfacial charge, were observed in the EVA/PE/EVA laminates.

3.3. EFFECTS OF VA CONTENT

The effect of different types of EVA on charge distributions in PE/EVA/PE laminates are demonstrated in Figure 3. PE/EVA 5/PE laminate (EVA 5 laminate) shows a positive charge peak in the PE layer at the cathode side and a negative charge peak in the PE layer at the anode side. PE/EVA 15/PE laminate (EVA 15 laminate) shows a negative charge in the PE layer at the cathode side and large interfacial charge peaks at the interfaces. On the other hand, PE/EVA 28/PE laminate (EVA 28 laminate) shows a broad positive charge peak in the PE layer at the cathode side, a negative charge peak in the PE layer at the anode side and interfacial charge peaks at the interfaces. Almost no charge is found in the bulk of the EVA in both EVA 15 and EVA 28 laminates.

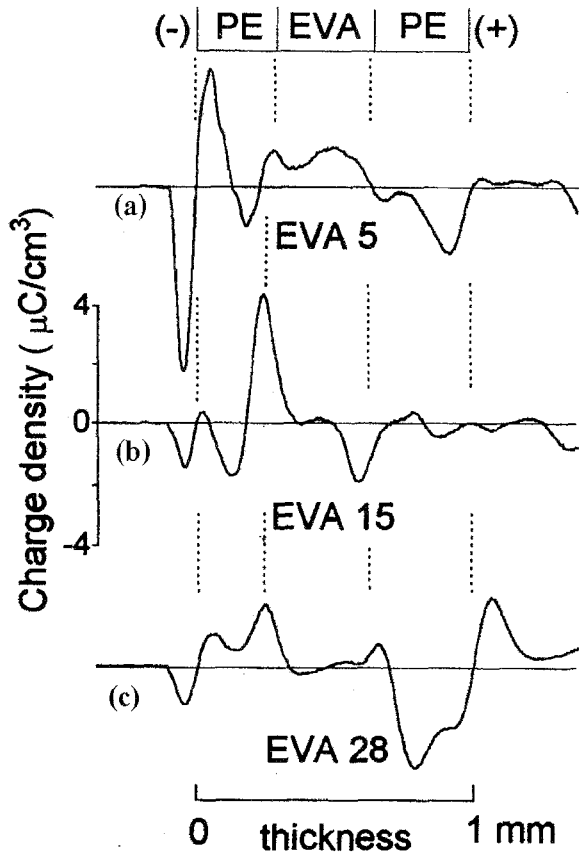


Figure 3. Effects of VA content in EVA on charge distributions at 40 kV immediately after short circuiting in PE/EVA/PE laminates. (a) EVA 5, (b) EVA 15, (c) EVA 28.

Charge distributions in these laminates measured during the application of 20 kV, corresponding to an average electric field of 20 kV/mm in this case, are shown in Figure 4. A relatively uniform electric field distribution is observed in the EVA 5 laminate compared to other laminates. The electric field in the EVA layer becomes smaller and the difference in electric fields between the PE and EVA layers becomes larger when the VA content in the EVA layers increases. Typical differences at an average electric field of 20 kV/mm are 7 kV/mm for EVA 5 laminates, 13 kV/mm for EVA 15 laminates and 23 kV/mm for EVA 28 laminates. All these results indicate that the internal electric field is highly distorted due to the charge accumulated at the interfaces and this distortion becomes larger when the VA content in the EVA increases.

3.4. EFFECTS OF INTERFACE MODIFICATION

Figure 5 shows the charge and field distributions in the laminates for which the interface has been modified by coating with chemicals such as silicone oil and crosslinking coagent (CA). In this Figure, (a) shows the charge distributions immediately after short circuiting (40 kV) and (b) shows the charge and electric field distributions at 20 kV during voltage application. The charge distribution of a control EVA 15 laminate is included for comparison.

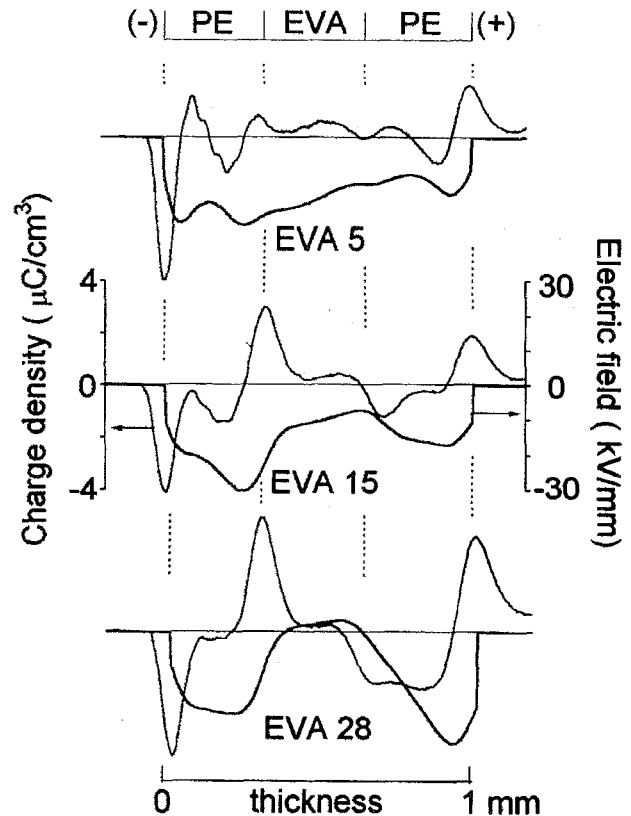


Figure 4. Effects of VA content in EVA on charge and field distributions at 20 kV during the voltage application in PE/EVA/PE laminates. (a) EVA 5, (b) EVA 15, (c) EVA 28.

As shown, large interfacial charge peaks remain after the discharge. The shape of the charge distributions in the laminates containing the silicone oil is very similar to that of the control EVA 15 laminate. However, two positive interfacial charge peaks are found at both interfaces of the laminate containing the CA. The electric field distributions in Figure 5(b) show a distortion of the electric field distribution due to the interfacial charge. In all laminates, the electric field in the PE layer is higher than that in the EVA layer. The difference in electric field between the PE and EVA layers is largest in the PE/EVA 28/PE laminate. In the laminate containing the CA, the electric field at an average field of 20 kV/mm reaches 30 kV/mm in the PE layer near the cathode and 2 kV/mm in the EVA layer.

Figure 6 shows the charge distribution in PE/EVA double layer laminates treated at 80 and 100°C for 10 min and for 1 h. Positive charge is observed in all PE layers, the magnitude of which increases with the applied voltage. Positive interfacial charge peaks are observed at the PE/EVA interfaces of all laminate samples. Since 100°C is high enough to melt the EVA, the EVA layer is expected to provide a good contact with the PE layer. It is of interest to note that the magnitude of the interfacial charge does not increase with the applied voltage. It is expected that the electric field distribution would be distorted due to interfacial charge. The present result suggests that the interfacial charge remains unchanged by heat treatment of the laminates at 100°C for 1 h. This observation

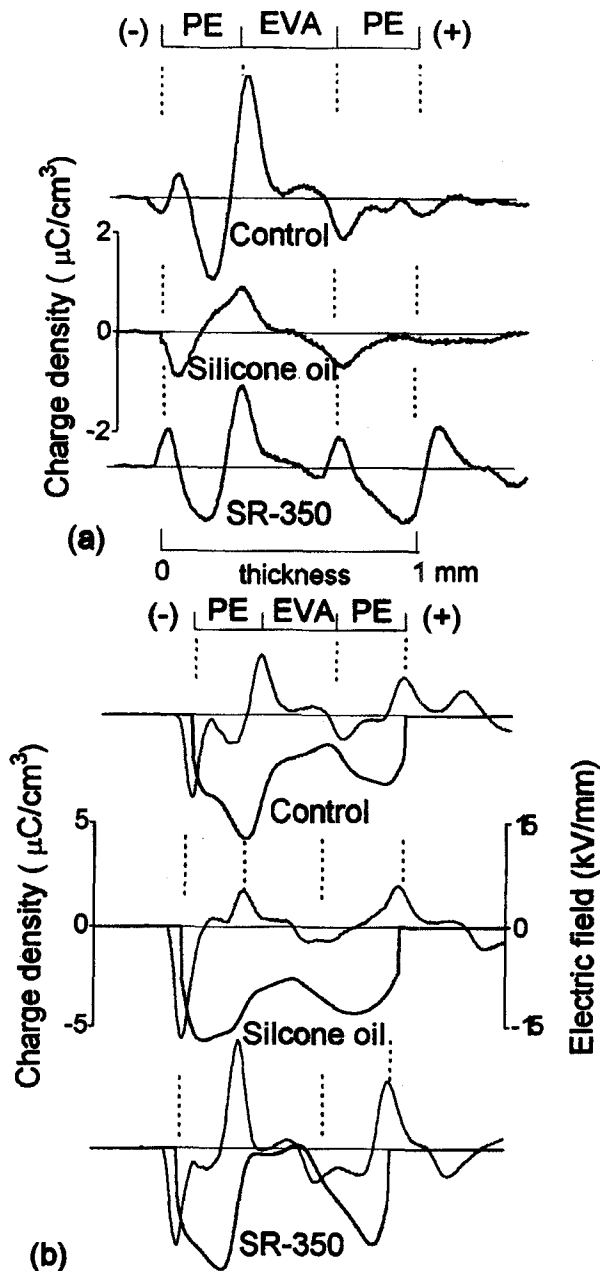


Figure 5. Effects of chemical coating on charge and field distributions in PE/EVA 15/PE laminates: (a) charge distributions at 40 kV immediately after short circuiting, (b) charge and field distributions at 20 kV during the voltage application: Silicone oil (top), pressed (middle), trimethylolpropane trimethacrylate (SR-350; bottom).

is contradictory to the observation with PE laminates [18] in that almost no interfacial charge was observed in PE laminates following heat treatment at 100°C for 1 h.

3.5. PE/EVA BLENDS

Charge distributions of PE/EVA blends are shown in Figure 7. It is found that the addition of EVA to PE reduces the heterocharge in PE. For example, the PE/EVA 28 blend containing 1% VA shows heterocharge which is smaller in magnitude than for pure PE. Only

a small amount of charge is found in PE/EVA 28 blend containing 4% VA.

A decrease of heterocharge near the cathode is seen more clearly in Figure 8, where the charge near the cathode is plotted as a function of EVA content (a) and VA content (b). The dependence of the charge near the cathode on EVA content shows a negative deviation from a simple additivity rule. This deviation becomes larger as the VA content in EVA increases. When the charge is plotted as a function of the VA content, all data seem to fit a single curve although some scatter in data points is found. The simple additivity rule does not take into account the effects of the interface between the PE and EVA phases, so the negative deviation from the simple additivity rule indicates that the interfaces play an important role in reducing the charge near the cathode in the blends.

Figure 9 shows scanning electron microscope pictures of the cross-section of cryofractured PE/EVA blends. The EVA phase was removed by extracting in toluene at 50°C for 24 h [19]. It is found that both blends, 1 and 4 VA, have the 'sea-island' morphology when EVA 15 or EVA 28 is blended with PE. The sea is the PE, the island is the EVA. No particular features were observed in PE/EVA 5 blends because the EVA phase dominates the blend. Since no co-continuous morphology is observed, two facts can be deduced. One is that there exist interfaces between PE and EVA phases, and the other is that the charge developed at these interfaces during voltage application does not dissipate freely through the more conductive EVA phases. The presence of interfaces in the blends will result in interfacial charge at the interfaces, which in turn leads to a distortion of the local electric field. The distortion of the internal field occurs in the direction of increasing the local electric field in the PE component, as observed with the laminates.

4. DISCUSSION AND SUMMARY

It was found that all PE/EVA laminates showed interfacial charge regardless of VA content in the EVA and regardless of interface modification. The interfacial charge develops not only by a Maxwell-Wagner interfacial polarization occurring in systems where the permittivity and electrical conductivity differ, but also by the accumulation of charge at each layer and at ill-characterized interfaces where there are defects such as voids.

Measured values of material parameters such as permittivity and electrical conductivity are listed in Table 1. The thickness of each layer of the laminate is 0.35 mm. In this situation, the interfacial charges at interfaces A, C, I and II of PE (-)/EVA/PE (+) laminates (Figure 10) can be calculated using Equations (1) to (4) under the assumptions of isotropic and uniform electric field.

$$Q_A = \frac{\epsilon_P}{t} V \quad (1)$$

$$Q_C = -\frac{\epsilon_P}{t} V \quad (2)$$

$$Q_I = V \frac{\sigma_E \epsilon_P - \sigma_P \epsilon_E}{t(\sigma_P + 2\sigma_E)} \quad (3)$$

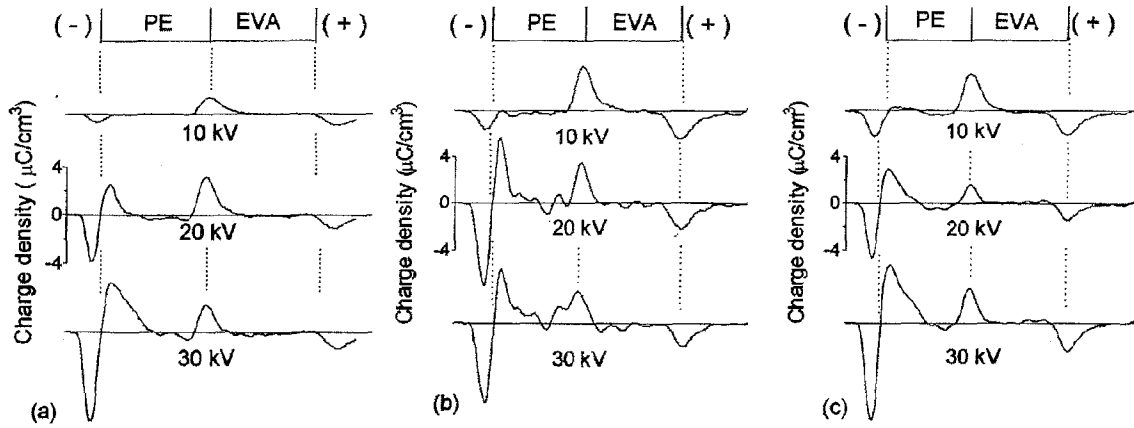


Figure 6. Effects of heat treatment on charge distributions in PE/EVA laminates: (a) 80°C, 10 min, (b) 100°C, 10 min, (c) 100°C, 1 h.

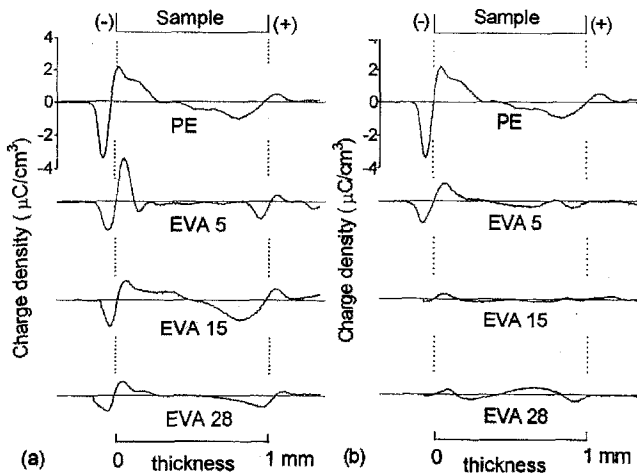


Figure 7. Charge distributions of PE/EVA blends immediately after short circuiting (40 kV).

Table 1. Permittivity ϵ , electrical conductivities σ , calculated interfacial charge Q_I and measured interfacial charge Q_{MI} , Figure 4. $t = 0.35$ mm, Area of electrode 7.07×10^{-4} m², $V = 20$ kV

| sample | ϵ | σ S/m | Q_I μC | Q_{MI} μC | Q_I/Q_{MI} |
|--------|------------|-----------------------|------------------|---------------------|--------------|
| PE | 2.2 | 2.0×10^{-14} | | | |
| EVA 5 | 2.28 | 9.5×10^{-13} | 0.0765 | 0.0159 | 4.81 |
| EVA 15 | 2.38 | 1.1×10^{-11} | 0.0788 | 0.0770 | 1.02 |
| EVA 28 | 2.84 | 2.7×10^{-10} | 0.0790 | 0.1128 | 0.70 |

$$Q_{II} = V \frac{\sigma_P \epsilon_E - \sigma_E \epsilon_P}{t(\sigma_P + 2\sigma_E)} \quad (4)$$

where ϵ , σ , t and V are permittivity, electrical conductivity, thickness of layer and voltage, respectively. Subscripts P and E stand for PE and EVA. Q_A , Q_C , Q_I and Q_{II} are calculated interfacial charges at anode, cathode, interfaces I and II , respectively.

Table 1 compares calculated Q_I and measured Q_{MI} interfacial charges at interface I . The interfacial charge at interface II was not considered because of two reasons: One is that the magnitude of interfacial charge at interface II should be identical to that at interface I because the EVA is sandwiched by two PE sheets. The

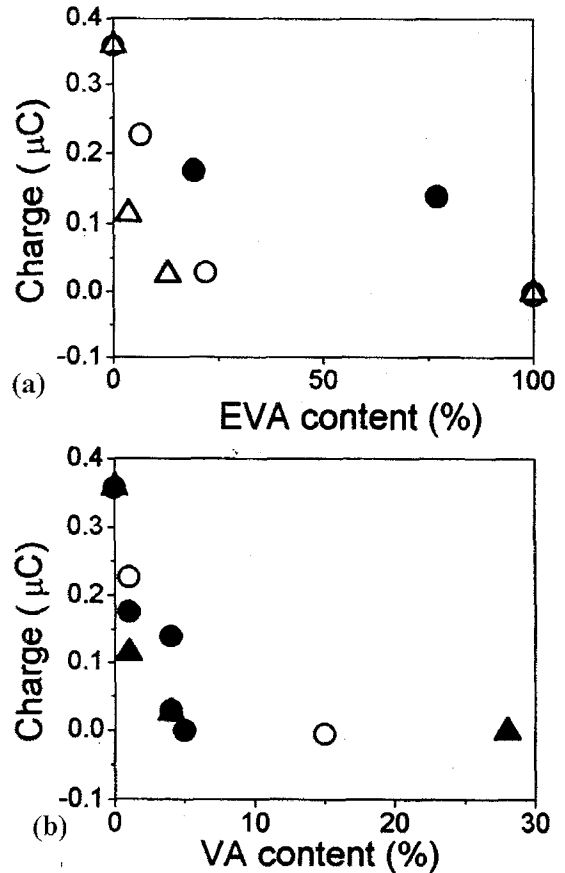


Figure 8. Charge near the cathode of PE/EVA blends immediately after short circuiting (40 kV): As a function of EVA content (a) and VA content (b). EVA 5 (●), EVA 15 (○), EVA 28 (▲).

other is that the attenuation of signal generated at the anode side is so significant that the interpretation of data is not meaningful.

As shown in Table 1, Q_I is almost the same, regardless of VA content in the EVA, whereas Q_{MI} increases with an increase of VA content in the EVA. The ratio of two interfacial charges, Q_I/Q_{MI} , decreases from 4.81 for PE(-)/EVA 5/PE(+) laminate to 0.70 for PE(-)/EVA 28/PE(+) laminate with an increase of VA content in the EVA.

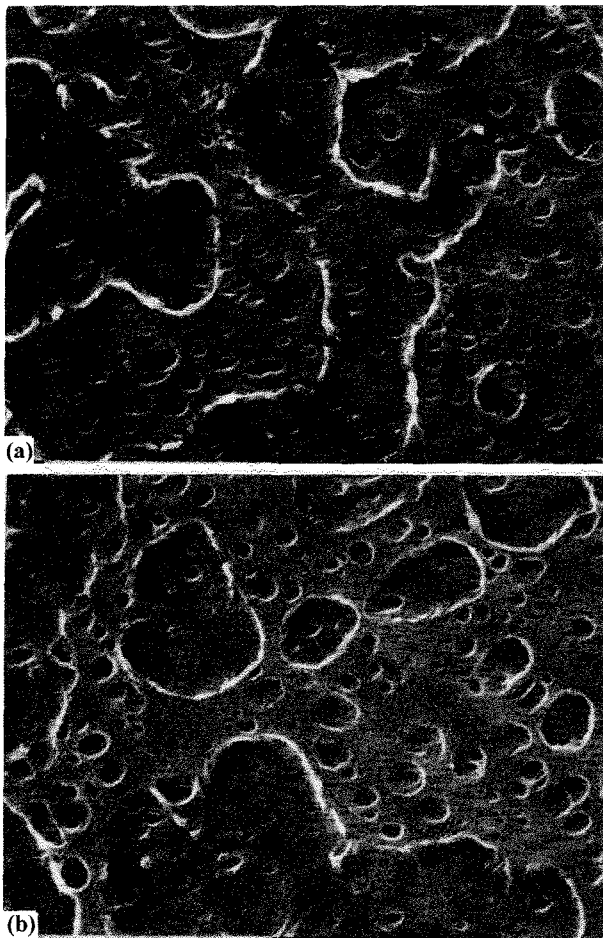


Figure 9. Scanning electron microscope pictures of cryofractured PE/EVA blends. (a) VA content in blend 1%, (b) VA content in blend 4%. (a) EVA 15, (b) EVA 28.

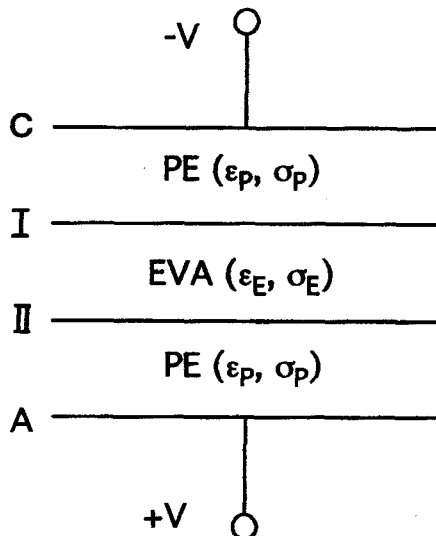


Figure 10. Three layer laminate (PE-/EVA/PE+) used for the calculation of interfacial charge.

Speculatively, $Q_{MI} \neq Q_I$ originates from the charge trapped at each layer and ill-characterized interfaces such as voids. As shown

in Figure 1, the amount of positive space charge accumulated in the EVA decreases with an increase of VA content in the EVA. The equations assume no space charge in the bulk of each layer, which holds true only for the EVA having high VA content in the EVA. These trapped charges should modify boundary conditions and consequently interfacial charges.

The heat treatment of laminates and the chemical coated on the surface of EVA were found to change the magnitude of interfacial charge in the laminates. The interpretation of these results is not simple because various aspects have to be considered. For example, the heat treatment could change not only the interface adhesion but also the morphology, such as crystallinity, of PE and EVA. The change of crystallinity of both PE and EVA could change the flow of charge, resulting in a change of interfacial charge. In the case of chemicals, the details of the chemicals are not known at this moment. These facts make the interpretation of the observed results very difficult. Nevertheless, the present results indicate that the interfacial charge can change due to the chemicals coated on the surface of the EVA, whereas the interfacial charge remains after heat treatment at 100°C for 1 h.

All PE/EVA laminates showed interfacial charge and consequently the local electric field is considerably distorted. The laminate results showed much higher electric fields in the PE layers than in the EVA layers, from which we can expect that the local field in the PE phase of the blends should be much higher than in the EVA phase in the blends. However, the observation was that the electric field distribution in the blends is relatively uniform. The reason for this could be that the PE and EVA phases are mixed so closely that the local electric fields are averaged out, resulting in a relatively uniform field distribution. Another feature is that the heterocharge decreased as the EVA content in the blends increased. The high local electric field in the PE phase could enhance the homocharge injection from the electrodes. This homocharge compensates the heterocharge existing in the PE, the net result being a decrease of heterocharge in PE/EVA blends with the increase of EVA content.

In summary, PE shows heterocharge while the EVA shows a broad distribution of positive charge of which the amount decreases with increasing VA content in the EVA. When PE and EVA are laminated, most charge develops at the PE/EVA interfaces. The interfacial charge could be modified by coating chemicals on the interfaces. This interfacial charge remains after heat treatment at 100°C for 1 h. The formation of interfacial charge was explained by a classical Maxwell-Wagner interfacial polarization mechanism. The interfacial charge distorts the local electric field distribution such that the electric field in the PE layers is higher than in the EVA layers. This distortion becomes greater when an EVA having higher VA content is laminated with PE. The heterocharge in the PE/EVA blends decreases as the VA content of the blends increases. We attribute this to an enhanced charge injection in the PE phase via an increased electric field in the PE phase.

ACKNOWLEDGMENT

This work was partly supported by the Electrical Engineering and Science Research Institute (95-7), Korea.

REFERENCES

- [1] S. Nagasaki, H. Matsubara, S. Yamanouchi, M. Yamada, T. Matsuike and S. Fukunaga, "Development of Water-tree-retardant XLPE Cables", IEEE Trans. Power App. Syst., Vol. 103, pp. 536-544, 1984.
- [2] H. Fugakawa and Y. Yasho, "Development of a New Insulation Material for DC Cables", Comm. BIII-2, JiCable 84, pp. 283-287, 1984.
- [3] K. S. Suh, *Thermally Stimulated Currents of PE/Ionomer Blends*, PhD Dissertation, University of Connecticut, USA, 1987.
- [4] M. Nawata, H. Kawamura and M. Ieda, "Effects of Additives on dc Treeing Breakdown in Polyethylene under Divergent Fields", IEEE Trans. Electr. Insul., Vol. 25, pp. 527-534, 1990.
- [5] K. S. Suh, D. Damon and J. Tanaka, "Space Charge in Polyethylene/ionomer Blends", IEEE Trans. Dielectr. El., Vol. 2, pp. 1-11, 1995.
- [6] Y. Suzuoki, G. Cai, T. Mizutani and M. Ieda, "Effects of Interface on Electrical Conduction in PE-EVA Composites", J. Phys. D: Appl. Phys., Vol. 17, pp. 141-146, 1984.
- [7] N. Hozumi, T. Okamoto and T. Imazo, "Space Charge Accumulation and Decay at the Interface between Polyethylene and Ethylene-vinylacetate Copolymer", Proc. 8th ISH, Yokohama, Japan, pp. 115-118, 1993.
- [8] G. Cai, "Evaluation of Internal Electric Field of PE/EVA Composite System by TSC-separation Methods", IEEE Trans. Electr. Insul., Vol. 25, pp. 702-706, 1990.
- [9] K. S. Suh, J. J. Lee, J. Y. Kim and T. Takada, "Charge Formation in PE/ethylene-based Copolymer Laminates", Proc. 8th ISH, Yokohama, Japan, pp. 111-114, 1993.
- [10] K. S. Suh, J. Y. Kim, C. R. Lee and T. Takada, "Charge Distributions in Polyethylene/ethylene Vinylacetate Laminates and Blends", IEEE Trans. Dielectr. El., Vol. 3, pp. 201-206, 1996.
- [11] T. Mizutani, Y. Suzuoki and M. Ieda, "Thermally Stimulated Currents in Polyethylene and Ethylene-vinyl-acetate Copolymers", J. Appl. Phys., Vol. 48, pp. 2408-4213, 1977.
- [12] K. S. Suh, J. J. Lee, J. H. Park and T. Takada, "Charge Formation in PE/polymer Laminates", Proc. 1993 CEIDP, Pocono Manor, Pennsylvania, USA, pp. 203-208, 1993.
- [13] K. S. Suh, J. H. Koo, S. H. Lee, J. K. Park and T. Takada, "Effects of Sample Preparation Conditions and Short Chains on Space Charge Formation in LDPE", IEEE Trans. Dielectr. Electr. Insul., Vol. 3, pp. 153-160, 1996.
- [14] T. Mizutani, T. Tsukahara and M. Ieda, "The Effects of Oxidation on the Electrical Conduction of Polyethylene", J. Phys. D: Appl. Phys., Vol. 13, pp. 1673-1679, 1980.
- [15] P. Fischer and P. Rohl, "Transient Currents in Oxidized Low-density Polyethylene", Progr. Colloid Polym. Sci., Vol. 62, pp. 149-153, 1997.
- [16] K. Iida, J. S. Kim, S. Nakamura and G. Sawa, "Effects of Molecular Structure on Electrical Conduction in Low-density Polyethylene above its Melting Point", IEEE Trans. Electr. Insul., Vol. 27, pp. 391-398, 1992.
- [17] S. H. Lee, J. K. Park, J. H. Han and K. S. Suh, "Space Charge and Electrical Conduction in Maleic Anhydride Grafted Polyethylene", IEEE Trans. Dielectr. Electr. Insul., Vol. 2, pp. 1132-1139, 1995.
- [18] K. S. Suh, H. S. Noh and M. Lee, "Interfacial Conditions and Space Charge in PE Laminates", Proc. 1995 ISEIM, Tokyo, Japan, pp. 247-250, 1995.
- [19] I. Ray and D. Khastgir, "Correlation between Morphology with Dynamic Mechanical, Thermal, Physicomechanical Properties and Electrical Conductivity for EVA-LDPE Blends", Polymer, Vol. 34, pp. 2030-2037, 1993.

Manuscript was received on 15 March 1996, in final form 15 October 1996.