

# Space Charge Behavior of Acrylic Monomer-grafted Polyethylene

Kwang S. Suh, Ho Gyu Yoon

Korea University, Department of Materials Science, Seoul, Korea

Chang Ryong Lee, T. Okamoto

CRIEPI, Yokosuka, Japan

and T. Takada

Musashi Institute of Technology, Tokyo, Japan

## ABSTRACT

This report describes space charge behavior of polyethylene (PE) grafted with acrylic monomers such as acrylic acid (AA), methacrylate (MA), ethylacrylate (EA) and n-butyl acrylate (NBA). The specimens were 0.7 mm thick with semicon electrodes, and vacuum degassed. Heterocharge is found in ungrafted control PE. This heterocharge decreases with the increase of AA content when AA is grafted onto the PE chains. This was attributed to an enhanced charge trapping at carbonyl sites provided by AA. When other acrylic monomers are grafted, heterocharge of the control PE increases first at low graft ratios and then decreases at higher graft ratios. This change was attributed to the combined effects of alkoxy groups acting as electron donating species and carbonyls acting as charge trapping sites. It seems that charge trapping at the carbonyls is sacrificed in part by the alkoxy groups at low graft ratios. All grafted polyethylenes are found at low fields below  $1 \times 10^5$  V/cm to obey the space-charge limited conduction (SCLC) mechanism. Effective charge mobilities of PE-g-AA and PE-g-NBA decrease with the increase of graft ratio while those of others remain unchanged.

## 1 INTRODUCTION

MODIFICATION of polyethylene (PE) to alter the electrical properties such as space charge behavior should be an important subject to the engineers working on the development of better insulating materials.

A permanent modification of electrical properties including space charge behavior of PE could be achieved by various methods such as the use of additives [1, 2], blending [3–5] and grafting techniques [6–8]. Of these, the additives, although they can alter the type of space charge in PE, disappear by the diffusion to the surface ('blooming-out' effect), resulting in an uncertainty in terms of a long-term reliability of the effectiveness of additives. The blending technique has been successfully employed to improve electrical properties of PE. Typical examples are the blends of PE with ethylene-based copolymers such as ethylene vinyl acetate (EVA) and ionomers. This has also disadvantages in that the microscopic interfaces generated at the interfaces between the components could cause interfacial phenomena due to the space charge accumulated at the interfaces and consequently a distortion of electric field distribu-

tion inside the blends [9–12]. A relatively homogeneous incorporation of components can be achieved by grafting the component onto the PE chains. This process is relatively simple because the grafting reaction is completed in a screw extruder having a relatively good mixing capability.

Recently, this grafting technique was employed to improve electrical properties of PE. For example, one PE (PE-g-maleic anhydride-grafted (MAH)) has shown a monotonic decrease of heterocharge in PE with the increase of graft ratio [6]. Electrical properties such as water treeing resistance and breakdown strength of a few acrylate grafted PE also have been reported [8].

This work, a continuation of the previous work, deals with space charge behavior of acrylic monomer grafted PE. Monomers were grafted onto PE chains by a reaction extrusion technique using a twin screw extruder. Acrylic monomers such as AA, MA, EA and NBA, and their space charge distributions were measured using a pulsed electroacoustic (PEA) method.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 MATERIALS

LDPE without any additives was used as a raw material for the grafting modification in the study. This LDPE, a product of Hanyang Chemical Co., Korea, has a density of  $0.920 \text{ g/cm}^3$  and a melt index of  $2.0 \text{ g/10 min}$ . Acrylic monomers such as AA, MA, EA and NBA and dicumyl peroxide (DCP) were purchased from Junsei Chemical Co. and used as received. Their chemical structures are given in Figure 1.

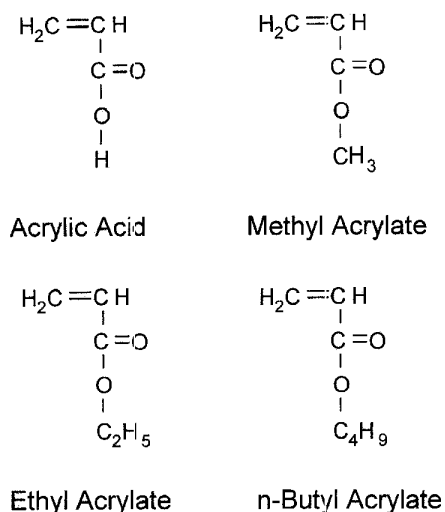


Figure 1. Chemical structures of acrylic monomers used in this study.

### 2.2 MODIFICATION REACTION AND ANALYSIS

Details of grafting reaction have been reported in the previous publications [6, 8]. A twin screw extruder was used for the grafting reaction; the schematic diagram of the grafting process shown in Figure 2. Rotating speed of the extruder was 15 rpm and the temperature of the barrel was set at 165 to 200°C. DCP content for the grafting reaction was fixed to be 0.02 parts per hundred resin (phr). All components were premixed in a Henschel mixer before they were fed into the twin screw extruder. Grafted PE was washed by immersing in proper solvents and then dried at 70°C for 24 h in a vacuum oven before they were subjected to tests. The solvents were methanol for both AA and MA, chloroform for EA and butanol for NBA.

It was experimentally confirmed whether or not the monomers were successfully grafted onto the PE chains. First, grafted PE extrudates were dissolved in boiling xylene for 4 h and then recrystallized by a proper solvent. Thus obtained grafted samples were washed again by flushing with fresh solvents and then dried at 70°C for 24 h in a vacuum oven. Figure 3 shows FTIR spectra of selected grafted samples. The monomers have their own IR characteristic peaks which indicate the existence of the monomers. As shown, each monomer contains carbonyl (C=O) groups, the environment of which varies depending on the sample. The  $1714 \text{ cm}^{-1}$  peak is for the carbonyl in carboxylic acid (-COOH)

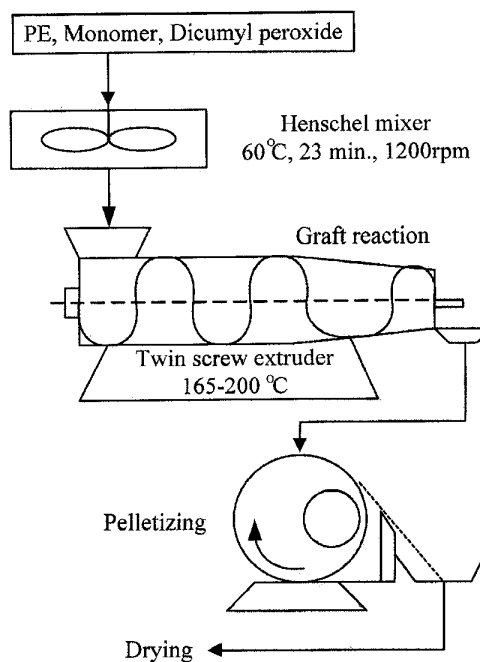


Figure 2. Preparation of grafted PE.

group of AA, the  $1720 \text{ cm}^{-1}$  is the carbonyl in MA and EA, the  $1740 \text{ cm}^{-1}$  peak is for the -COO- in MA, EA and NBA. The presence of these peaks in the solvent-washed samples is an indication that the monomers were successfully grafted onto the PE chains.

The graft ratio  $r$  was determined by both elemental analysis and FTIR. A calibration curve was first obtained from both elemental analysis and FTIR spectra for a series of grafted samples. Peak heights were read from appropriate peaks of the FTIR spectra and graft ratios were then determined by reading the value in a calibration curve.

### 2.3 MEASUREMENTS OF SPACE CHARGE DISTRIBUTIONS

Charge distributions were measured by a PEA method, the measurement principles and techniques of which are described elsewhere [13, 14]. It consists of an electric pulse generator (pulse width 10 ns, pulse height  $-2 \text{ kV}$ ), HV source ( $+100 \text{ kV}_{\text{dc}}$ ), a test cell with a piezoelectric detector, and a data acquisition system. The piezoelectric detector was made of  $9 \mu\text{m}$  thick polyvinylidene fluoride (PVDF) film. Samples for space charge density measurements were prepared by compression molding at  $130^\circ\text{C}$  for 10 min. The thickness of the grafted PE samples was typically  $0.7 \text{ mm}$  and that of the semicon electrodes was typically  $0.2 \text{ mm}$ . The voltage was applied for 30 min and then the sample short circuited. Immediately after short circuiting ( $< 3 \text{ min}$ ), the charge distribution was measured, meaning that the charge distributions shown in this report are the profiles of charge remaining after the discharge.

EVA-based semicon electrodes were prepared by curing at  $180^\circ\text{C}$  for 20 min using a Carver Laboratory hot press. In order to avoid the effects of constituents in the semicon electrodes, the semicon films were

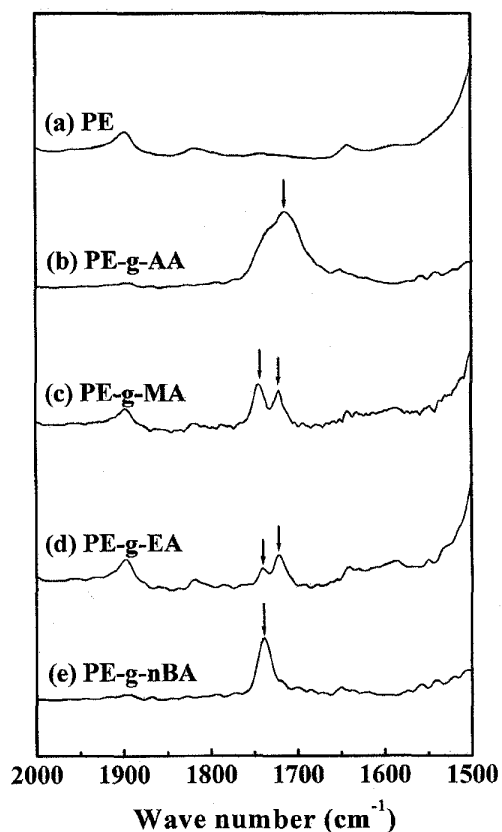


Figure 3. FTIR spectra of selected grafted PE.

vacuum degassed at 80°C for 100 h before being used as electrodes. The same type of semicon electrodes were also used throughout the study.

### 3 RESULTS AND DISCUSSION

#### 3.1 CHARGE DISTRIBUTIONS IN LDPE

Figure 4 shows charge distributions of a raw material, LDPE for grafting modification. As shown, heterocharge, *i.e.* positive charge near the cathode and negative charge near the anode, was observed. This heterocharge could be due to the migration of additives and impurities remaining in the control PE. It has been reported that low molecular weight PE chains could also contribute to the formation of heterocharge [15].

The present charge distributions were obtained by semicon electrodes made of a mixture of olefinic polymer, conductive carbon black, antioxidant and processing aids. Previous studies have suggested that the types of electrode materials change space charge accumulation in PE including LDPE and crosslinked polyethylene (XLPE). For examples, Chapeau *et al.* found homocharge with a vacuum evaporated metal electrode while heterocharge with a conductive silicone grease electrode in LDPE [16]. Sanden reported the different charge accumulation behavior depending on the types of electrode materials in XLPE [17, 18]. All these results suggest that the charge behavior in LDPE and XLPE could

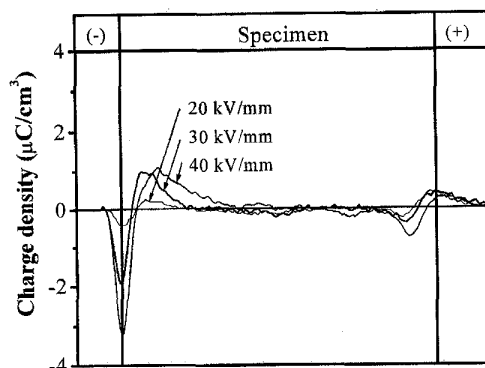


Figure 4. Charge distributions of control PE at various voltages.

Table 1. Maximum heterocharge  $Q$  and graft ratios  $r$ .

Material	$r$ %wt	$Q$ $\mu\text{C}/\text{cm}^2$
PE-g-MA	0.013	0.048
PE-g-EA	0.018	0.034
PE-g-NBA	0.105	0.017

alter when a different electrode material is employed. Since the present work is centered at the development of insulating materials for power cables, the semicon electrodes made of shielding materials for power cables were selected as an electrode material.

#### 3.2 CHARGE DISTRIBUTIONS IN GRAFTED PE

Figure 5 shows charge distributions of selected grafted PE. As shown, charge distributions of grafted PE are different depending on type and amount of monomers. For example, PE-g-AA shows small homocharge (negative charge near the cathode), whereas heterocharge (positive charge near the cathode) is found in all other samples. In this case, the magnitude of heterocharge is different depending on the type and amount of monomers. Figure 6 shows the charge near the cathode as a function of graft ratio. It appears that PE-g-AA samples show a monotonic decrease of heterocharge with the increase of graft ratio and finally homocharge is seen at high graft ratios above 0.1 to 0.15 %wt of AA. All other grafted PE show an increase of heterocharge at low graft ratios and then decrease of heterocharge at higher graft ratios. Amount of heterocharge and graft ratio where the heterocharge is the largest are different depending on the type of monomer, as summarized in Table 1. One can see that, as the number of carbon of substituents in acrylic monomers increases, graft ratio showing maximum heterocharge increases while maximum heterocharge decreases.

A monotonic decrease of heterocharge in case of PE-g-AA samples indicates that carbonyl introduced onto the PE chains by the grafting reaction acts as an effective charge trapping site. An increase of homocharge by the trapping of injected charge should result in a decrease of heterocharge. However, this cannot explain the observations with other grafted PE.

Carbonyls in acrylic monomers can act as charge trapping sites and heterocharge forming sites. Its charge trapping ability will be reduced substantially as heterocharge forming ability increases. This holds true

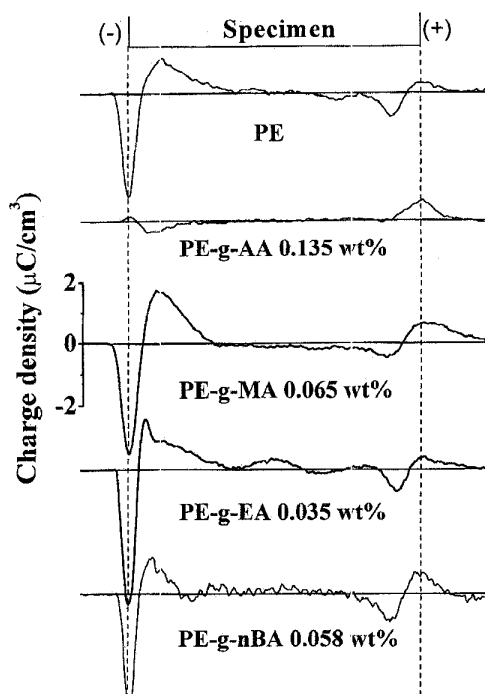


Figure 5. Charge distributions at 40 kV/mm of selected grafted PE.

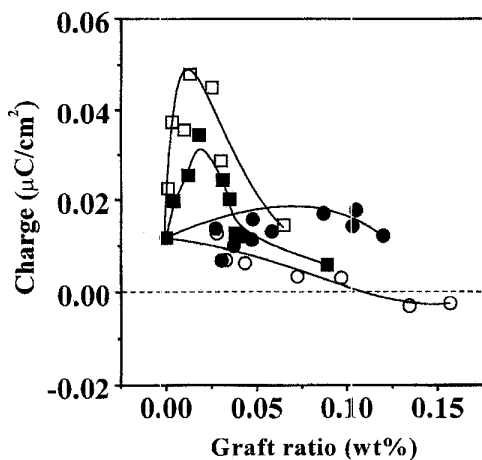


Figure 6. Charge near the cathode as a function of graft ratio: PE-g-AA (○), PE-g-MA (□), PE-g-EA (■), and PE-g-NBA (●).

when alkoxy groups are present near the carbonyls. Since electron donating ability increases as the number of carbons of substituents increases, *i.e.* methoxy (-OCH<sub>3</sub>)→ethoxy (-OC<sub>2</sub>H<sub>5</sub>)→butoxy (-OC<sub>4</sub>H<sub>9</sub>). In this case, heterocharge formation by the orientation dominates over homocharge formation by charge trapping. As far as the orientation is concerned, bulkier substituents will become more difficult, with the net result being smaller heterocharge as the size of substituents. On the other hand, as the concentration of carbonyls becomes higher, charge trapping ability dominates over the orientation, resulting in an increase of homocharge by an increased charge trapping capability. In this case, heterocharge decreases at higher acrylic monomer contents.

Since the voltages used in this study were low, compared to other results [19], an extensive homocharge formation is not expected. Therefore, experiments with the same samples at higher voltages are needed. Nevertheless, the present results suggest that the type of space charge accumulated in PE could be altered by grafting proper monomers.

### 3.3 CONDUCTION CHARACTERISTICS OF GRAFTED PE

Figure 7 shows *J-E* curves of (a) PE-g-AA and (b) PE-g-EA. Compared to the ungrafted control PE, the PE-g-AA (graft ratio = 0.03 %wt) shows similar *J* at low fields while lower *J* at high fields. Current densities decrease even more considerably at higher graft ratio (graft ratio = 0.16 %wt). This result indicates that charge migration is suppressed in PE-g-AA, which increases with the increase of AA content. It is attributed to the increase of AA acting as charge trapping sites. The same type of decrease in *J* with the increase of graft ratio was observed in PE-g-NBA. However, both PE-g-EA and PE-g-MA did not show this trend.

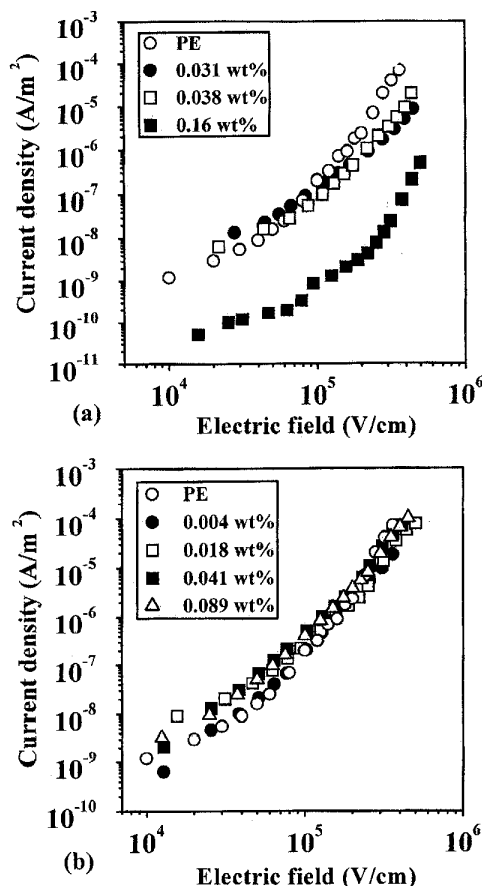


Figure 7. *J-E* curves of (a) PE-g-AA and (b) PE-g-EA.

One of the classical ways to identify the conduction mechanism is to examine the linearity of *J-E* curves. The slope of *J-E* curves in Figure 7 is 2.0 at electric fields to  $1 \times 10^5$  V/cm, although a slight difference is observed depending on the samples. This slope becomes  $>2.0$  at higher

fields. When  $J$ - $E$  curves show linearity, the samples obey a trap-free space-charge-limited conduction SCLC mechanism [20]. In this case, according to Child-Lambert law,  $J$  shows the  $-3$  power dependence on the sample thickness.

In order to clarify the conduction mechanism of PE-g-AA (0.031 %wt graft ratio), a thickness dependence of  $J$  was examined at two voltages, e.g., 300 V ( $0.6 \times 10^5$  V/cm) and 700 V ( $1.4 \times 10^5$  V/cm). The results in Figure 8 show a  $-3$  power dependence of  $J$  vs. sample thickness, which indicates that this sample obeys the trap-free SCLC mechanism. This holds true for all acrylate-grafted PE samples at electric fields of up to  $\approx 1 \times 10^5$  V/cm.

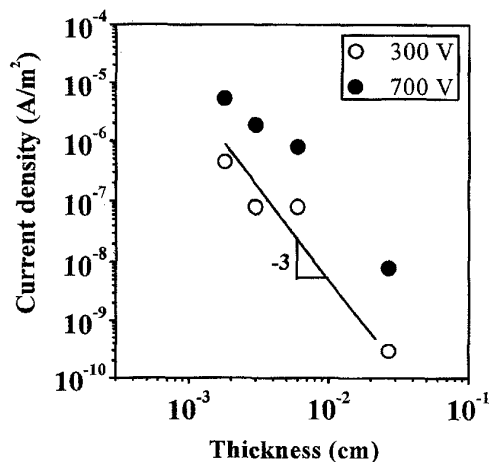


Figure 8. Thickness dependence of current density of PE-g-AA (AA content: 0.031 %wt).

Other conduction mechanisms such as Schottky and Poole-Frenkel effects were checked by examining the field dependence of current density or conductivity and comparing the permittivities estimated from the slopes. However, the permittivities obtained from the slopes, i.e. Schottky and Poole-Frenkel coefficients, did not agree with the values of LDPE and grafted PE. Therefore, both Schottky and Poole-Frenkel mechanisms were excluded.

By assuming that the samples obey the trap-free SCLC mechanism, effective charge mobilities at low fields of selected grafted PE were estimated from the Child-Lambert Law. Some results are shown in Figure 9. Both PE-g-AA and PE-g-NBA samples show a decrease of effective charge mobility with the increase of graft ratio, whereas both PE-g-MA and PE-g-EA samples show no such decrease of effective charge mobility with the increase of graft ratio.

#### 4 CONCLUSIONS

UNGRAFTED control PE shows heterocharge. PE-g-AA shows a monotonic decrease of this heterocharge and finally homocharge is observed at high graft ratios, which was attributed to the increase of charge trapping at AA sites. Other grafted PE show an increase of heterocharge at low graft ratios and then a decrease at higher graft ratios. Maximum heterocharge appears at higher graft ratios with the increase of number of carbons of substituents of acrylic monomers. This was explained by a role of electron donating alkoxy and carbonyl groups. At

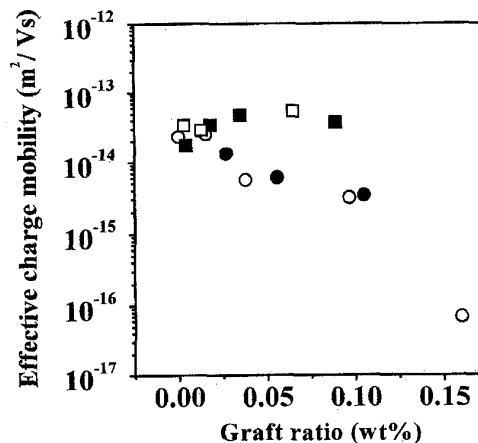


Figure 9. Effective charge mobilities as a function of graft ratio: PE-g-AA (○), PE-g-MA (□), PE-g-EA (■), and PE-g-NBA (●).

low graft ratios, charge trapping ability of carbonyls is reduced in part by the effect of alkoxy groups - electron donating groups, so that heterocharge formation by the orientation dominates. In this case, the orientation becomes harder with the increase of the size of substituents. At higher graft ratios, charge trapping dominates over the orientation, resulting in a decrease of heterocharge. Heterocharge could also enhance homocharge injection. These grafted PE are found at low fields below  $1 \times 10^5$  V/cm to obey the SCLC mechanism. With the increase of graft ratio, effective charge mobilities in both PE-g-AA and PE-g-NBA decrease while those of PE-g-MA and PE-g-EA remain unchanged.

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