Space charge suppression effect of nano-size fillers added to polymeric materials

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Abstract. Space charge suppression mechanism in nano-composite polymer material is studied using experimental results and numerical simulation. Recently, many kinds of nano-composite polymeric materials have been reported to have improved their characteristics under high electric field. For example, LDPE/MgO nano-composite, which is made up of low density polyethylene (LDPE) and nano size filler of magnesium oxide (MgO), exhibits high volume resistivity and high dielectric strength under dc electric field. Authors have investigated the space charge behaviour in LDPE/MgO nano-composite under high electric field using pulsed electro-acoustic (PEA) method. It has been found that, compared to LDPE, the space charge formation is also suppressed in the nano-composite material. As a reason for the suppression, we have suggested that the induced dipole polarization around MgO filler formed by dc stress application might play a role of carrier trap sites. From the numerical calculation, distortion of electric potential around MgO is seen to be much larger than that around naturally included dipole. It means that the MgO acts as a deep trap site as different from some defect or ions included in LDPE. Using the numerical calculation based on such electric potential distortion, we have tried to simulate the space charge distribution in LDPE/MgO under high dc electric field. The simulation results are in good agreement with the experimental results.

1. Introduction
Polymer nano-composites have drawn researchers’ attention as next generation insulating materials [1-3]. Addition of small amount only of a nano sized filler to a base polymer, electrical properties of the composite material are drastically improved. For example, LDPE/MgO nano-composite, which is made up of low density polyethylene (LDPE) and nano size filler of magnesium oxide (MgO), shows high resistivity and dielectric strength under dc electric field [4, 5]. Furthermore, authors have found that space charge accumulation is also drastically suppressed under high dc electric field in LDPE/MgO nano-composite. Authors have been investigating the space charge behavior in LDPE under very high dc electric field of more than 100 kV/mm using the pulsed electro-acoustic (PEA) method [6]. Under such stress, what is called a ‘packet-like charge’ [7, 8], is injected from an electrode and it distorts electric field distribution in bulk of LDPE significantly. In some cases, the distorted electric field distribution has a maximum value of twice the applied average electric field, and often a breakdown occurs in the sample [8]. Earlier, authors have given some explanation for such
packet-like charge behavior numerically [9]. However, under same test conditions as that of LDPE, the packet-like charge doesn’t appear in the LDPE/MgO nano-composite [10]. It means that the nano-composite material is very reliable material for use under high dc electric field. However, the mechanism of the suppression has not been clear yet. Considering the improvement in electrical properties, Prof. Tanaka et.al. [11] have proposed that, a “multi-core” zone induced on the surface of nano filler may play a role of such drastic change. However, by only such explanation, it is hard to understand the suppression of space charge accumulation in LDPE/MgO under high dc stress. Therefore, authors have tried to explain it in terms of the induced dipole around additional filler in polymers under dc electric field [12]. In this paper, authors try to show the comparison between numerical simulations based on such idea and typical measurement results.

2. Space charge accumulation in nanocomposite films

2.1. Space charge accumulation in LDPE and LDPE/MgO under high dc stress.

At first, the difference between space charge accumulations in LDPE and LDPE/MgO nano-composite is briefly introduced. All samples are supplied from J-power systems Corp. Figure 1 shows typical space charge measurement results using PEA system under dc high electric fields of 100, 150 and 200 kV/mm. In this figure, time dependent space charge profiles are described using color chart. In the color chart, the red and blue colors stand for the positive and the negative charge densities, respectively. The color bar described beside the data shows the scale of charge density for color chart. In this figure, the vertical axes stands for the time after voltage application in minutes. The horizontal axis stands for the position in the bulk of sample. Left (blue) and right (red) vertical lines show the positions of induced charges on the cathode and the anode, respectively. The thickness of samples is about 70 µm. In the case of LDPE/MgO nano-composites, the added amounts of MgO are 0.2 and 1 phr (parts per hundred parts of resins: LDPE/MgO 1 phr means 100g LDPE mixed with 1g MgO).

When the average electric fields of 100 kV/mm is applied to the samples, only induced charges are observed in all samples at the interfaces between samples and electrodes. On the other hand, a large amount of “packet-like charges” is observed in LDPE under 150 and 200 kV/mm. Positive packet-like charge is injected form the anode and they move towards the cathode slowly in both cases. Since the packet-like charge gradually increases with time, it deforms the electric field distribution in bulk of the sample. The enhanced maximum electric field sometimes shows the value of twice or more of the initially applied average electric field. However, almost no such significant space charge is observed.
in LDPE/MgO (1 phr) even under applied average electric field of 200 kV/mm. In the case of LDPE, a breakdown sometimes occurs by the enhancement of the electric field. It means that the breakdown by such electric field enhancement hardly occurs in LDPE/MgO nano-composite. From these results, we found the addition of nano size MgO filler to LDPE shows a suppression effect for charge injection under dc stress. Details of the charge accumulation characteristics in LDPE and LDPE/MgO nano-composites are described elsewhere [10].

2.2. Space charge distributions in LDPE/MgO - Dependence on electric field

When a high electric field such as 200 kV/mm is applied to LDPE/MgO (1 phr), almost no significant space charge injection is observed. However, a small amount of space charge accumulates in bulk of LDPE/MgO (1 phr) under relatively low applied electric field. Figure 2 shows space charge distributions under applied electric fields of (a) 50 kV/mm and (b) 250 kV/mm.

![Figure 2. Space charge distributions dependence on applied electric field in LDPE/MgO (1 phr) under electric fields from 50 to 250 kV/mm.](image)

As shown in Fig. 2 (a), a small amount of positive homo space charge is observed. The shape of the space charge distribution is not packet-like but it distributes as it permeates into bulk of the sample. The permeated edge of the distribution is about 20 \( \mu \text{m} \) from the anode electrode. On the other hand, in the case of 250 kV/mm, such homo space charge is not observed while a small amount of hetero space charge is observed near cathode side. It is curious that the positive charge injection from anode is observed under low electric field while it is not observed under high applied electric field. To show the dependence clearly, figure 2 (c) shows a comparison of space charge distributions under various electric fields. Since the initial induced charge density on the electrode is proportional to the applied electric field, it is difficult to compare the shapes of the charge distributions. Therefore, the distributions Fig. 2 (c) are normalized using the peaks of the negative charge densities on cathode. Referring to Figure 2 (c), it can be seen that with the increase in the applied electric field, the edge of the distribution becomes closer to the anode surface. In other words, the charge injection suppression effect in LDPE/MgO nano-composite is more effective under higher applied electric field.

3. Induced dipole polarization

Authors have proposed that the filler added to base resin acts as an “induced dipole” under dc electric field and it works as a trap site in LDPE [12]. This phenomenon is derived from the difference of permittivity between base resin and filler. Figure 3 shows schematic models of electric field distributions around the filler [12]. In this figure, \( E_0 \) and \( \sigma_p \) stand for an applied electric field and induced charge density, respectively, on the surface of the filler. Below the figures of electric field distributions, the electric potential distributions around the filler are also described. In this figure, \( V_0(r) \) and \( V(r) \) stand for a potential distribution of applied voltage and distorted potential distribution by the existence of the filler (“potential well distribution”). In the case of figure 3 (a) when the permittivity of the base resin (\( \varepsilon_1 \)) is same as that of filler, no charge is induced at the interface between them. In this case, the electrical potential distributions \( V_0(r)+V(r) \) and potential well distributions \( V(r) \) are flat. On the other hand, in this case of dielectric filler has higher permittivity (\( \varepsilon_2 \)) than that of base resin as
shown in Fig. 3 (b), dipole charge $\sigma_p$ is induced on the interface of the filler according to the following equation:

$$\sigma_p(\phi, \theta) = \varepsilon_0 E_0 \left( \frac{\varepsilon_2 - \varepsilon_1}{2\varepsilon_1 + \varepsilon_2} \right) \cos \phi \sin \theta$$

(1),

where $\phi$ and $\theta$ stand for the angles in spherical-coordinate system. This equation is written as the filler has a complete spherical shape. In the model shown in Fig. 3, the direction of applied electric field $E_0$ is the direction with angles of $\phi = 0$ and $\theta = +90$ degree. As a result, negative charge induced left side, and same amount of positive charge induced other side. The potential well distributions $V(r)$ is calculated from difference between electrical potential distributions $V_0(r)$ and applied electric potential $V_0(r)$. As shown in this figure, it is found that the electric field around the filler is distorted and a potential well is generates around the filler. Figure 3 (c) shows that the filler is conductive. In this case, the potential distribution has distorted much larger than that around the dielectric filler. We thought case (b) phenomena occurred in LDPE/MgO nano-composite. Since the potential well is generated around the dielectric filler under dc applied electric field, the injected carriers must be trapped around the filler.

4. Electric field and potential distortion around nano filler

Here, a practical calculation of the potential distortion around MgO nano filler in LDPE is carried out. Figure 4 shows the electric field distribution around MgO filler and an electron. In this calculation, the electron is supposed as a charged defect or impurity included in LDPE. The distributions are produced by assuming that, for example, the MgO has a spherical shape with diameter of 50nm under applied electric field of dc 100 kV/mm. The values of 2.3 and 9.8 are used as the relative permittivities of
LDPE and MgO in this calculation. Since the effective cross-section area for the carriers passing around the MgO is much larger than electrons, the potential well formed around MgO is able to capture the carriers than that by the charged defect or impurity. Furthermore, the potential well around MgO collects many carriers while the electron is able to capture only one positive charge. The applied electric field depends on the effective cross-section area. In other words, when the higher electric field is applied, the larger area is effective for trapping the carriers around the filler.

**Figure 4.** Electric field distortion around MgO filler and an electron produced by induced surface charge of a spherical MgO (diameter 50nm) under dc 100kV/mm and an electron.

To show the image of effective cross-section area for trapping clearly, a 3D schematic diagram of electric potential distribution is described in Figure 5. In this figure, two typical cases of three dimensional electric potential distributions around MgO filler are described. Figure 5 shows the potential distributions around MgO under (a) 100 kV/mm and (b) 250 kV/mm. In this figure, green and blue lines stand for the equipotential lines of negative 0.1 and 0.5 eV, respectively. It is easy to understand that the cross-section area of 0.1 eV formed around MgO under dc 250 kV/mm is much larger than that under 100 kV/mm. Furthermore, assuming MgO in the film shape material between parallel plane electrodes, the positive and negative potential wells are formed on both sides of MgO facing to the cathode and the anode sides, respectively. It means that the positive and negative carriers injected from anode and cathode are always captured with the negative and positive potential well formed around MgO filler, respectively. In other words, MgO filler under applied dc electric field acts as both positive and negative trap site.

**Figure 5.** 3D electric potential well around MgO fillers produced by induced surface charge of a spherical MgO filler (diameter 50nm) under DC stress (a) 100kV/mm and (b) 250kV/mm.
5. Numerical analysis of suppression effects by nano fillers

Here, we try to simulate the charge distribution in LDPE/MgO nano-composite under various dc electric fields. In this simulation, we assume the cross-section area with potential of larger than 0.5 eV as the effective trapping area. For example, when the applied electric field is 100 kV/mm, the trapping area means the inside of the blue equipotential line shown in Fig. 5 (a). The calculated cross-section area of it is about 2700 nm$^2$. For example, when the content of MgO is 1 phr, numbers of MgO nano fillers is about 38 per 1 $\mu$m$^3$ and average distance between MgO fillers is about 333nm. In this simulation, we assume that the injected carrier move according to the electric field and it doesn’t pass through the effective trapping area.

Figure 6 shows simulation results of trapping areas in LDPE/MgO (1phr). In this figure, each square shows a view of a layer in bulk of the sample with a distance of 1, 3 and 5 $\mu$m from charge injection surface. In each square, the white and black areas show where the carrier is captured by the well and where carrier can pass through the layer, respectively. It means that each white square pattern show the effective trapping area around MgO filler. Please note that the effective trapping area is shown using a square pattern for ease of calculation. Since the actual MgO filler is dispersed randomly, the white square pattern also put in each layer randomly. Here, since we assume the carrier can not pass through the effective trapping (white) area, the passing area (black) gradually decrease with increase the distance from the injection surface as shown in Fig. 6. It is found that the each size of the white square pattern under dc electric field of 50 kV/mm is smaller than that under 250 kV/mm. It means that the cross-section of the effective trapping area under 50 kV/mm is smaller than that under 250 kV/mm. Since the each size of the white square pattern under electric field of 50 kV/mm is small, there still remains black area even at the distance of 5 $\mu$m away form the injection surface. Under the electric field of 250 kV/mm, however, there is almost no such black area at the distance of 5 $\mu$m away from the injection surface. By the simulation, we can calculate the injection depth of the space charge from the injection surface. Figure 7 shows the calculated injection depth under various applied electric field. It is found that the injected carrier under electric field of 50 kV/mm can pass through the bulk of the sample for more than 20 $\mu$m while the injected carrier under 250 kV/mm cannot pass through even for 5 $\mu$m. From this simulation results, it is clearly found that the injected carrier can be mobile under lower applied electric field for longer distance from the injected surface. Furthermore, the simulation result seems to be close to the experimental result show in Fig. 2. The edge of the injected charge distribution under electric field of 50 kV/mm is located at the distance of about 20$\mu$m from the injected electrode and the distance becomes shorter with increase of the applied electric field.

![Figure 6. Simulation results of trapping areas in LDPE/MgO 1phr. Vertical axis: depth from electrode.](image)

![Figure 7. Space Charge trapping ratio by potential well. Vertical axis: injection depth from electrode.](image)
the simulation was carried out based on parameters with rough assumptions, it is not a precise result. However, since we can have such very close simulation result to the experimental result even with such rough assumption, we think the basic proposed idea for the charge injection suppression effect by adding MgO nano filler to LDPE is a meaningful explanation.

6. Conclusion
Space charge formation in LDPE/MgO nanocomposite film subjected to a high electric field greater than 100kV/mm has been studied using PEA system and numerical simulation. When a high electric field was applied to LDPE, a huge amount of positive charge is injected into bulk and the charge accumulation distorts local electric field strongly. On the other hand, in LDPE/MgO nanocomposite film, which is including only less than a few wt% of MgO filler, no space charge formation is observed even under such severe applied electric field. To explain the difference in space charge formation, we proposed a trapping model of “induced dipole polarization”. On the basis of this model, we showed the followings.

1. Induced dipole polarizations of nanoparticles subjected to a high electric field are enough to become trapping site for carriers.
2. Injection depth and the effective trapping by the induced dipole around the added nano filler depend on the difference between relative permittivities of nanoparticle and base resin. They also depend on applied electric field, too.
3. Under more than dc electric field of more than 100 kV/mm, the lower applied electric field can make a longer space charge injection depth in LDPE/MgO (1 phr) nano-composite.
4. The simulation for injection depth of injected charge shows a good agreement with the experimentally measured charge distribution using PEA system.

7. References
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