Calculation and Analysis of Two Level Traps Model in Polymeric Materials

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***Abstract*—Space charge formation in polymeric materials can cause some serious concern for design engineers as the electric field may severely be distorted, leading to part of the material being overstressed, resulting in material degradation and possibly premature failure at the worst. It is therefore important to understand charge generation, trapping, and detrapping processes in the material. Trap depths and concentration of materials are important as they are potentially related to microstructure of the material. Changes in these parameters may reflect aging taken place in the material.**

In the present paper, characteristics of charge trapping and detrapping in low density polyethylene (LDPE) under dc electric field have been investigated using the pulsed electroacoustic (PEA) technique. A simple trapping and detrapping model based on two trapping levels has been used to qualitatively explain the observation. Numerical simulation based on the above model has been carried out to extract parameters related to the material. It has been found that trap depths and concentration of both shallow and deep traps show significant differences for the sample with different periods of electric field application. Besides, the trap energy levels of these shallow and deep traps are compared with the values in literature to evaluate the model. The results indicate that trap depths and concentration of both shallow and deep traps may be used as aging markers as changes in the material will certainly affect trapping characteristics (trap depth and concentration).

***Index Terms*— Ageing, polymer, space charge, traps.**

I. INTRODUCTION

SPACE charge formation in polymeric materials can cause some serious concern for design engineers as the electric field may severely be distorted, leading to part of the material being overstressed. At the worst, this may result in material degradation and possibly premature failure.

A thorough understanding the dielectric properties of polymeric insulating materials is important to efficiently and safely utilize the materials in both power and electronic industries. Recently, the phenomenon of charge trapping and detrapping has attracted significant attention, since charge characteristics of the insulating material may be closely related to the aging taken place in it [1, 2].

However, to determinate the trapping parameters and characteristics of the material is not easy. Thermally stimulated currents (TSC) technology is one of an efficient measuring method to determinate the trapping parameters [3], but it is a destructive method which could alter morphologic features of the material due to heating. The development in space charge mapping techniques [4] in the past few decades has resulted in an abundant knowledge resource on space charge, and one of the most popular methods is the pulsed electroacoustic (PEA) measurement. One of the advantages of the PEA method is a non-destructive measurement which is safe for the insulation of the material, so it is more convenient and possible for the condition monitoring of the insulating states of power equipments. There are a large number of papers about the PEA measurement and its space-charge profile description, but space-charge accumulation and the related trapping-detrapping phenomena are still poorly understood [5]. One of the techniques to characterize traps is to investigate the time characteristics of charge trapping and detrapping.

In our previous paper [6], a theoretical model based on shallow and deep traps has been proposed to describe the space dynamics considering both trapping and detrapping process. In this paper, a quantitative analysis of the trapping parameters and characteristics has been calculated using our experimental data via PEA measurement on LDPE samples. The results indicate that trap depths and concentration of both shallow and deep traps may be used as ageing markers as changes in the material will certainly affect trapping characteristics (trap depth and concentration).

II. MODEL OF TWO LEVEL TRAPS

Trapping and detrapping are closely related to the trap distribution in terms of spatial and energy. For a semicrystalline polymeric material, it is possible that traps may have several discrete energy depths or even continuous energy distribution. Spatially, trap distribution may vary for a sample as the material may experience different processes including physical, thermal, and chemical treatment. This is especially true for the

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region near to the surface. To simplify the mathematics involved here we assume that the traps are uniformly distributed across the sample and only have two trap energy levels, i.e., one representing shallow trap and another for deep trap.

The trapping model can be described by three processes as following: charge injection, trapping, detrapping and kinetics of trapping and detrapping process, respectively. To simplify the model, the trapping process from shallow to deep trap and the detrapping process from deep trap to shallow trap are not considered in the present study. In addition, we assume the trapped charges are close to the injecting electrode, so the recombination with the injected charge from the opposite electrode can be neglected. The details of the model description can be found in [6].

In this paper, the emphasis is placed on charge decay after removing the applied field. The detrapping process after the removal of applied field is as follow.

$$n_1(t) = n_{10}\exp(-k_1 t) \quad (1)$$

$$n_2(t) = n_{20}\exp(-k_2 t) \quad (2)$$

Where n_{10} and n_{20} are the initial trapped charges in shallow and deep trap at the moment when the applied field is removed, respectively.

The total trapped charge density during detrapping process is given by

$$n(t) = n_{10}\exp(-k_1 t) + n_{20}\exp(-k_2 t) \quad (3)$$

Where k_1 and k_2 are the thermal detrapping rate constants for shallow and deep traps respectively.

The thermal detrapping rate constant can be express as

$$k_{th} = N_c v_{th}\sigma_c \exp\left(-\frac{E_t}{kT}\right) \quad (4)$$

Where N_c is the effective density of states in the conduction band, v_{th} is the thermal velocity of the charge, E_t is the trap depth, k is the Boltzmann constant, and T is the temperature.

The parameters k_1, k_2, n_{10}, and n_{20} are important as they are potentially related to microstructure of the material. Changes in parameters may reflect ageing taken place in the material. In details, k_1 and k_2 reflect two different levels of traps in the material which may be related to different kinds of chemical or physical defects in the material. Likeness, n_{10} and n_{20} reflect trap concentration of both shallow and deep traps. The above four parameters can be obtained via data from a series of space charge decay measurements for different stressing times.

III. EXPERIMENTAL RESULTS FROM LDPE

Space charge measurements were carried out on additive-free low density polyethylene (LDPE). The thickness of the film was ~180 μm. Details of the experimental can be found in reference [7]. Fig.1 and Fig.2 give the results of decay of space charge profiles and total charge for 10 minutes stressing times respectively. For comparing, charge decays after 2 minutes stressing was also tested and results will be discussed in the following section (not shown in Fig.1 and Fig.2).

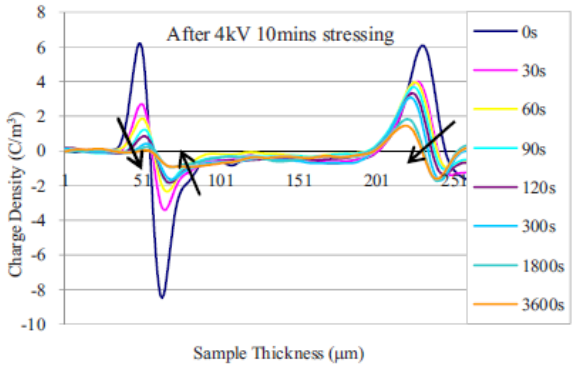

Fig.1. Space charge decay after the removal of the applied voltage 4kV for t= 10min

The total amount of charge in the bulk can be estimated using the following equation

$$Q = \int_0^d |\rho(x)| \cdot S \cdot dx \quad (5)$$

Where ρ(x) is charge density, S is the electrode area and d is the thickness of the sample. The value of ρ(x) is shown in Fig.1, and S and d used in this paper are 38.465 mm2 (radius of the electrode area is 3.5mm) and ~180μm, respectively. According to equation (5), the total trapped charge can be calculated and plotted in Fig.2.

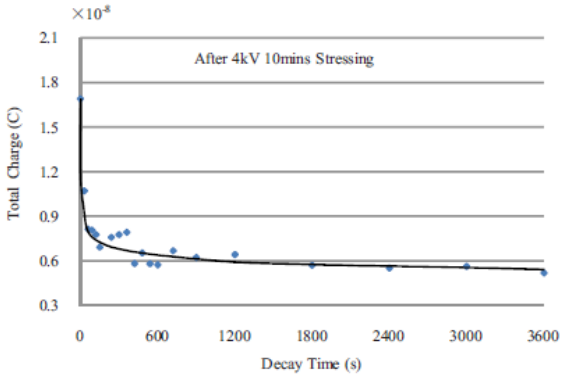

Fig.2. Decay of the total trapped charge after being stressed at 4kV for t=10min

It has been found that the total number of trapped charge $n(t)$ decreases fast at first and is followed by a slow decay. At last (about 1h's decay time), $n(t)$ comes to a stable value and changes little. It is indicated that there are two kinds of traps existed in the material as described in section 2. Details of the parameters of the two traps are analyzed in the following section.

IV. CALCULATION AND DISCUSSION

A. Calculation of Parameters in the Model

Numerical simulation is carried out to extract parameters from the model. The experimental data in section 3 can be fitted well with the model proposed. Fitting results of the calculation of the parameters k_1, k_2 are 0.02783~0.03276 and 8.68×10^{-5}~9.665×10^{-5}; and the parameters n_{10}, and n_{20} are

1.46×10^{10}~3.85×10^{10} and 7.26×10^{9}~3.06×10^{10}, respectively.

Similar simulation has also been carried out on the space charge data obtained from 2 minute stressing. It has been found that after 2 minutes stressing, both of shallow and deep trapped charge accumulate in the material, and the number of shallow trapped charges (n_{10}) is 20 times more than that of deep trapped ones (n_{20}). This demonstrates that charges are easier trapped in shallow traps than deep traps.

It can be shown that the thermal detrapping rate constants k_1 and k_2 have a significant difference numerically. k_1, which reflects the changing rate of shallow traps, are hundreds of times more than k_2, which stands for the changing rate of deep traps. It indicates charge decay faster from shallow traps than that from deep traps.

After 10 minutes stressing, the similar accumulation numbers of both shallow and deep trapped charges is found, besides, the number of both shallow and deep trapped charges increases comparing with that at 2 minutes stressing, but the ratio of shallow and deep ones decreases at 10 minutes stressing. This shows that more charges are trapped with longer stressing time, but the nature of charges trapped in the material would change after different stressing time.

In theory, the thermal detrapping rate constants of 2 minutes and 10 minutes stressing time should be of the same value. Our calculation results are agreeable to the theory. The values of both stressing time are of the similar, besides, the ratio of k_1 and k_2 at two different stressing time is almost the same.

B. Discussion

Since both physical and chemical defects may be present in insulating materials and both trap electrons. And different kinds of defects correspond to different defect trapping energy. It is necessary to acquire the trap depths of shallow and deep traps in the material presented in our model.

According to equation (4), the trap depth can be written as

$$E_t = kT\ln\left(\frac{N_c v_{th}\sigma_c}{k_{th}}\right) \tag{6}$$

If all parameters in equation (6) are known, then the trap depth of both shallow and deep traps can be calculated. Firstly, T and k_{th} can be determined according to our experimental data, k is the Boltzmann constant, N_c and v_{th} are also constants for a specific material, utilizing the results of other workers in this field, we use the following values: $N_c=10^{25}$, $v_{th}=10^{13}$ s^{-1}[8]. Depending on the type of defect, a bulk trap may capture an electron or a hole that has been injected into the material. Trapping centers are generally characterized by their ability to capture cross section, σ_c (m^2). Cross sections can be different based on the initial charge state of the centers, such as: coulombic attractive, neutral or coulombic repulsive. In our experimental results, there are two kinds of traps existed in the material, so this is the evidence of the existence of two capture cross sections strongly. Besides, cross section of shallow trap is larger than that of deep one. That is to say $\sigma_1>\sigma_2$, using the other measuring data by previous worker, the following values can be obtained for σ_1, σ_2 respectively, values 10^{-14}~10^{-18}[3, 9].

Using the fitting data of our experimental, the shallow and deep trap depth can be estimated. The trap depth estimated by us is as follows: E_{t1} (shallow trap) is of the value 0.4~0.6 eV, and E_{t2} (deep trap) 0.8~1.0 eV. It must be noted that the delay in the PEA measuring time immediately after the applied voltage was switched off does not allow us to detect shallower traps [2]. So our depth data obtained may be a little higher that existed other measuring data [10], but it does show that there are two types of traps in the material. This supports that there may be different defects which have its own trap depth.

The presence of both physical and chemical defects will lead to traps in the material having a range of trap depths. Due to aging or the presence of additives, it may lead to the accumulation of electrons in traps forming a relatively immobile space charge.

Physical defects may be created by changing of the morphological of crystallinity ratio, molecular weight, and microstructure. All these changes may lead to a trap energy modification and trapping or detrapping process [11]. Chemical defects may be created by photo-oxidation process which will change the chemical structure of the material. These changes also have some influences on the trap energy distribution and trapping or detrapping process.

Overall, shallow traps will have something to do with the physical defects while deep traps will be related to the chemical defects in the material. And in the experimental of this paper, the physical defects affect charging behavior stronger than the chemical defects for the material used in our study is additive-free LDPE, this is similar to the early research results using other space charge measuring of the trapping and detrapping properties of polymers in relation with their microstructure [12].

At the same time, results of the trap concentration of shallow and deep traps can be obtained from our experimental, as can been seen both shallow and deep traps charge increase with the time duration from our experimental analysis. The order of magnitude of the density of trapped charges in our calculation is agreeable to the results of other method using electroluminescence（EL）emission detection of the LDPE material [13].

According to our proposed new model, we can present the expression of the n_{10} and n_{20}, as expressed in equations (7) and (8) as following,

$$n_{10} = \frac{A_1 N_1}{A_1 + k_1}\{1 - \exp[-(A_1 + k_1)t]\} \tag{7}$$

$$n_{20} = \frac{A_2 N_2}{A_2 + k_2}\{1 - \exp[-(A_2 + k_2)t]\} \tag{8}$$

It can be also concluded that the trap charge increases with the increase of time duration. Furthermore, the shallow trapped charges were also relevant to parameters A_1, k_1, and N_1, and the deep trapped charges are related to A_2, k_2 and N_2. It is possible to compare the amount of N_1 and N_2 if knowing the above all parameters (A_1, A_2, k_1 and k_2). The thermal detrapping rate constants for shallow and deep traps k_1 and k_2 can be obtained from the space charge decay results directly. Now what is left is

the determination of A_1 and A_2. Considering the definition of A_1 and A_2 in our proposed model,

$$A_1 = \frac{J_0 \sigma_1}{q} \exp\left(\frac{E}{E_0}\right) \quad (9)$$

$$A_2 = \frac{J_0 \sigma_2}{q} \exp\left(\frac{E}{E_0}\right) \quad (10)$$

A_1 and A_2 can be estimated from the cross section values.

Obviously, the amount of shallow traps is more than that of deep ones for our additive-free LDPE samples. This is an agreement to the conclusion that shallow traps are related to physical defects while deep traps are related to chemical defects, since the samples used in our experiments are all unaged LDPE, which just exist physical defects but less chemical defects. These findings are agreeable to other studies that impurities are most likely to be present in HDPE, or XLPE, than in LDPE, meaning HDPE and XLPE can become more deep trapping sites than LDPE [12].

As can be seen that the trapped charges reflect the amount of both shallow and deep traps, if the time is long enough, N_1 and N_2 are proportional to n_{10} and n_{20} respectively. So the space charge measurement can be an effective and sensitive method to investigate the trapping characteristics. Different materials and different situation of materials under special conditions may show different trapping characteristics, which may not be seen from some regular chemical method such as infrared or Raman spectra but can be sensitive to the measurement of space charge [14].

V. CONCLUSION

From the decay of space charge of LDPE samples of different stressing time and our previous proposed new trapping model, the parameters of trapping characteristics are calculated and estimated including trap energy levels (trap depths) and number of traps (trap concentration) of both shallow and deep traps.

In LDPE, there are more numbers of shallow traps than deep traps due to its own physical structure. Since ageing may changes the chemical structure of the material and traps, further research will be concentrated on the ageing effect on these proposed parameters, which may be used as ageing markers for insulating state monitoring.

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