THERMAL AGEING AND ITS IMPACT ON CHARGE TRAP DENSITY AND BREAKDOWN STRENGTH IN LDPE

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Abstract: Low-density polyethylene (LDPE) has been widely used as power cable insulation, because of its good electrical performance and stable chemical characteristics. However, in recent years, with the rise of large-capacity and long-distance HVDC transmission systems, the effect of space charge has a significant impact on the insulation selection and design. Furthermore, the change in the electrical performance of insulation after ageing is also required to be understood. It has been reported that ageing leads to an increase in charge trap density. The increase of trap density in LDPE makes the transport of charge carriers between traps easier. Consequently, the electrical breakdown strength will also be affected. This paper focuses on the LDPE films with different degrees of thermal ageing and studies its impact on charge trap density and change in electrical breakdown strength. The ageing degrees of sample were characterized using Fourier-Transform Infrared (FTIR). Space charge dynamics were measured using the pulsed electroacoustic (PEA) technique. In addition, electrical breakdown strength of the aged samples was measured and breakdown data were processed using the Weibull distribution. The change in characteristic breakdown strength is related to the change in charge trap density. The results suggest that the change in charge trap density of an insulating material can be used to characterize electrical performance of the material, therefore, the ageing status.

1 INTRODUCTION

Space charge has been considered to be both causes and consequences of ageing in polymeric materials. During high voltage application, particularly for DC condition, space charge formation in insulation system can cause an amplification of the electric field at certain locations. Resultantly, it will accelerate degradation and even lead to an early failure of insulation materials [1]. Traps are charge capturing sites inside materials. Typically, traps at shallow and deep energy levels are respectively related with physical and chemical defects inside materials [2]. It has been reported that ageing leads to an increase in charge trap density. The increase of trap density in polymeric material makes the transport of charge carriers between traps easier. Meanwhile, the deep traps from ageing in the vicinity of the electrodes lead to electric field distortion [3]. In recent years, several space charge ageing models were proposed to describe the relation between the charge trap and insulation life [4-5].

In previous research, the ageing of low-density polyethylene (LDPE) film and cross linked polyethylene (XLPE) film taken from high voltage ac serviced cables which were in operation for up to 12 years were used to test a model for connecting the charge trap density and DC breakdown strength. Nevertheless the data collected from the retired cables are affected by several factors such as electrical, thermal or radiated influence. To modify and simplify the model, the control experiment on the insulation material with less influential factors is necessary. In this paper, attempt has been made to use the change in charge trap density in LDPE film to characterize electrical performance of the material, therefore, the ageing status.

2 SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

The normal and aged samples used for experiment were commercially available additive-free LDPE. The same group of samples were used in both pulsed electroacoustic (PEA) and DC breakdown test. So the thickness of the sample is ~100μm. LDPE films were thermally aged at 90 °C for 0, 1, 5, 10 and 15 days and at 100°C for 0, 1, 5, 10, 15 and 20 days in air with normal fan oven. All groups of LDPE were stored in the same environment.

2.1 FOURIER-TRANSFORM INFRARED (FTIR) SPECTRA

Fourier-Transform Infrared (FTIR) technique was applied to reveal the chemical properties for original and aged LDPE films. The spectrum was observed by the IR absorption in the range 440~ 4000 cm^{-1} through LDPE film using a spectrometer “IR Prestage-21”. The spectrum was observed by 32 scans accumulation, and the resolution was 4 cm^{-1}. Before the experiment, samples were cleaned using alcohol and then dried. Special

attention has been paid in the range of 1690~1800 cm^{-1} as the carbonyl group peaks due to thermal ageing should be observed [6]. The carbonyl index was calculated by a ratio between the oxidation peak A_{ox} and the area of invariant peak A_j [7]. i.e. carbonyl index (CI) *R* is:

$$R = \frac{A_{ox}}{A_j} \quad (1)$$

2.2 DC BREAKDOWN MEASUREMENT

DC electrical breakdown strength of the normal and aged samples was measured. In experiment, the prepared sample was sandwiched between two spherical electrodes of diameter 6.5mm. The external voltage was raised up with a ramp rate of 100V/s from zero. The testing protocol and procedure follow ASTM standard D3755-97 [8]. Moreover, in order to avoid flashover during the test, the sample and the two spherical electrodes were fully immersed in silicone oil. And for each type of sample, about 20 measurements were made to reduce statistical error. To analyse and describe DC breakdown behaviours, the breakdown data were processed using the Weibull distribution [9].

2.3 PULSED ELECTROACOUSTIC (PEA) MEASUREMENT

Space charge dynamics were measured using the pulsed electroacoustic (PEA) technique. The thickness of the sample was ~100μm. A drop of silicone oil was placed between LDPE film and both two electrode in order to make sure good acoustic propagation. The reference voltage was set at 1kV and all types of samples were stressed at an electric field of 40kV/mm. The PEA data were collected during volts-on for 1800s and volts-off for 1800s to explore both the injection and decay behaviours of space charge. The total amount of space charge in the bulk is estimated using the following equation.

$$Q = \int_0^d |\rho(x)| \times S \times dx \quad (2)$$

where: $\rho(x)$ = charge density (C/m^3)

S = electrode area (m^2)

D = thickness of the layer close to the cathode (m)

In our previous work, a model based on shallow and deep traps has been proposed to describe space charge dynamics [2]. Moreover, the number density of total trapped charge density during decay is given by following equation [3]:

$$n(t) = n_1(t) + n_2(t) = n_{10}\exp(-k_{th1}t) + n_{20}\exp(-k_{th2}t) \quad (3)$$

where $n_1(t)$ *and* $n_2(t)$ mean the number density of trapped charges in shallow and deep trap respectively. And the parameters k_{th1}, k_{th2}, n_{10}, and n_{20} are related to microstructure of the material. Changes in parameters may reflect ageing taken place in the material. In detail, k_{th1} and k_{th2} relate to two different trap depths. Consequently, all the values of charge amount versus time were curve-fitted using the two exponential expressions given in the equation below:

$$Q = a \cdot \exp(-b \cdot t) + c \cdot \exp(-d \cdot t) \quad (4)$$

3 EXPERIMENTAL RESULTS

3.1 FOURIER-TRANSFORM INFRARED (FTIR) RESULTS

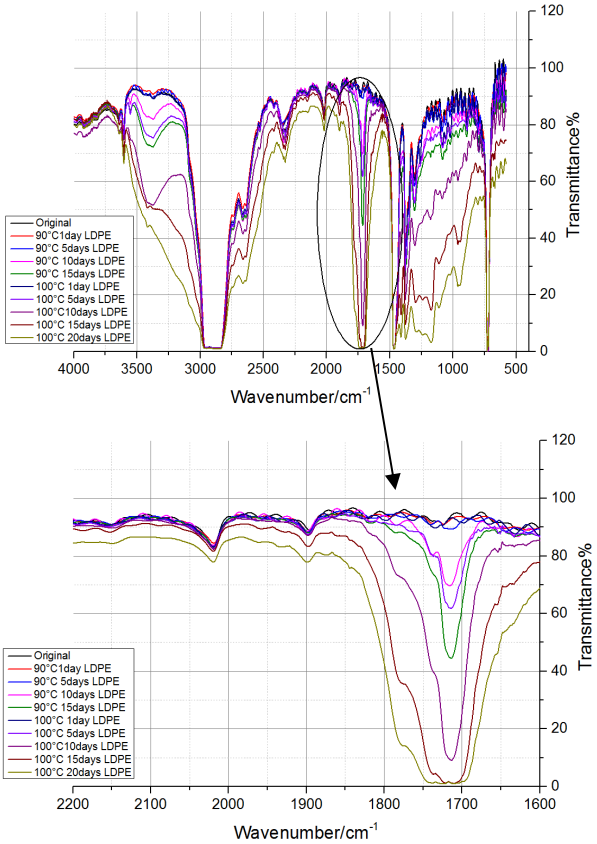


Figure 1: FTIR spectrum of original, 90°C aged and 100°C aged samples with zoom-in peaks within region 1600-2200cm^{-1}.

Figure 1 shows the change in FTIR spectra of LDPE due to thermo-oxidative treatment at 90°C and 100°C. Carbonyl index was calculated with equation (1) by taking the ratio of absorption bands at 1710 and 2020 cm-1.

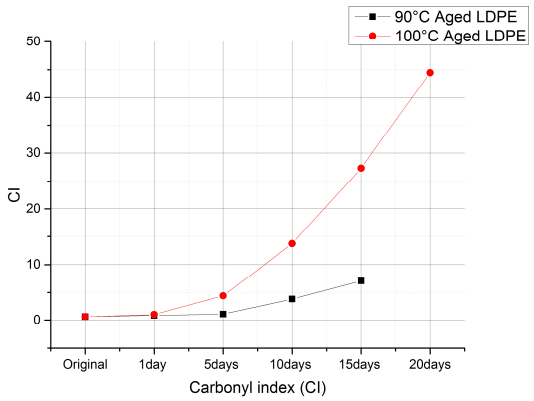
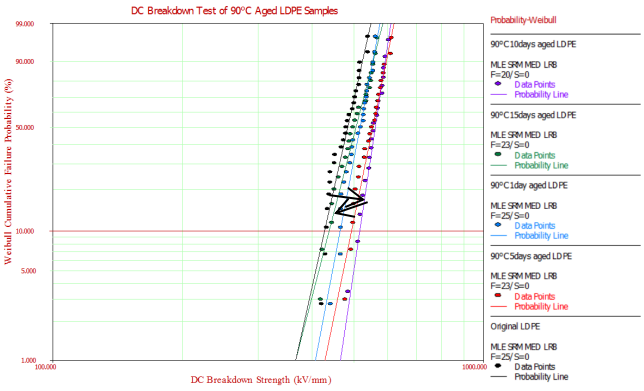


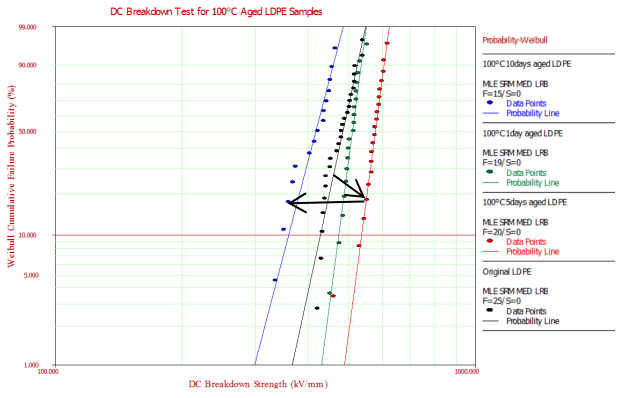
Figure 2: Change in the CI of 90°C aged and 100°C aged samples obtained from FTIR spectrum.

Figure 2 shows the change in the CI as a function of thermo-oxidation time. It can be seen that the CI increases exponentially after 1 day. Meanwhile, the CI rising rate for 100°C aged LDPE is faster than the index for 90°C aged LDPE after 1day.

3.2 DC BREAKDOWN RESULTS



(a)



(b)

Figure 3: The Weibull plots of the cumulative probability of breakdown versus breakdown voltages for 90°C aged and 100°C aged samples.

The thermo-oxidation has a strong impact on the electrical performance of LDPE insulation. The changes in electrical breakdown strength are closely associated with the concentration carbonyl groups when the samples were aged below the melting temperature (112°C) [10]. Normally, in the earlier model about the breakdown behavior of thermal aged LDPE, the breakdown strength of aged LDPE decreases as the ageing degree in-depth compared with the original LDPE [5]. Nevertheless, Figure 3 shows that the breakdown strength of both 90°C and 100°C aged samples increase initially up to 10 days at 90°C and 5 days at 100°C. Any further ageing will lead to a decrease in the breakdown strength.

3.3 PULSED ELECTROACOUSTIC (PEA) RESULTS

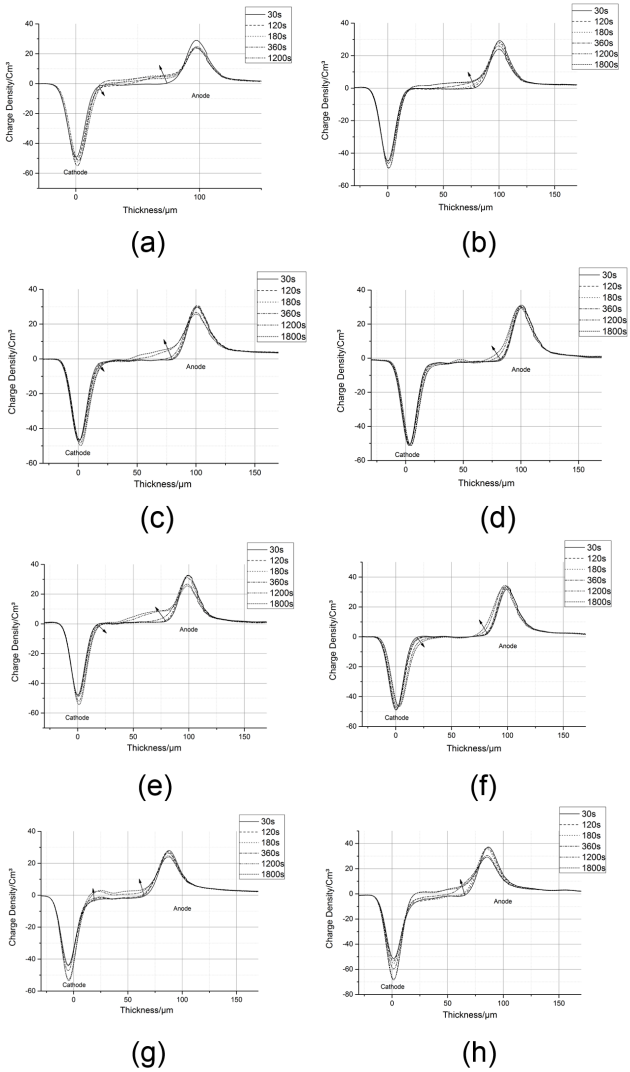
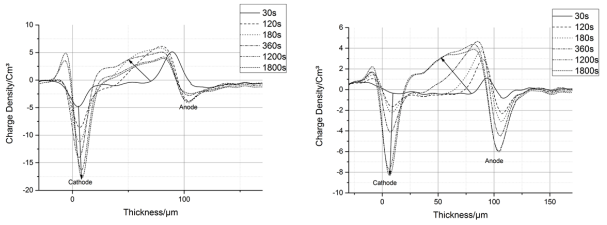


Figure 4: Space charge profiles over 1800s at 40kV/mm in original LDPE (a), 90°C 5 days aged LDPE (b), 90°C 10 days aged LDPE (c), 90°C 15 days aged LDPE (d), 100°C 5 days aged LDPE (e), 100°C 10 days aged LDPE (f), 100°C 15 days aged LDPE (g), 100°C 20 days aged LDPE (h).

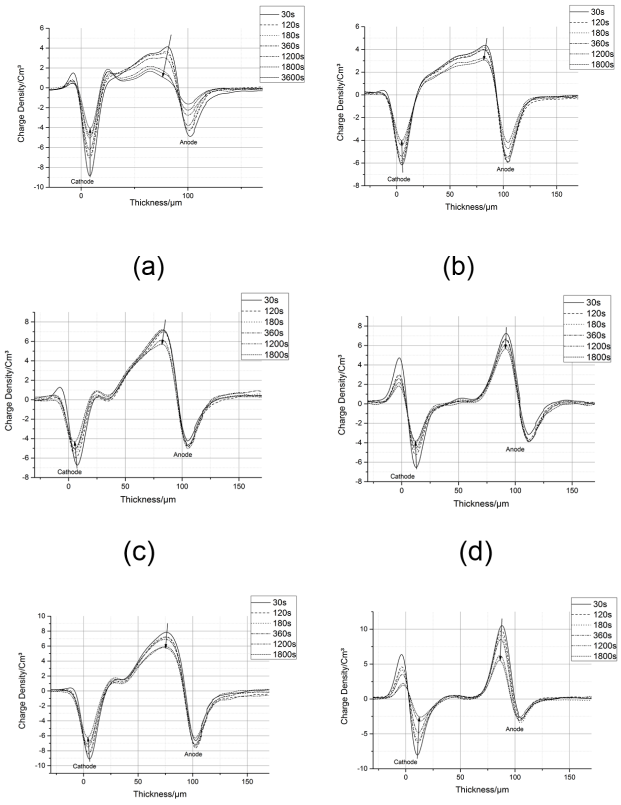
In order to explore the evolution of space charge during injecting period, space charge profiles were observed over 1800s, so we cannot assume there

is no recombination between the injected charge carriers. Meanwhile, the positive and negative charges in the sample cannot be separated as the PEA measures the net charge. As a result, the focus has been paid to the charges in the vicinity of the electrodes [10]. It is observed in Figure 4 that the rate of charge injection in the vicinity of the electrodes decreases, compared with the original LDPE. Compared between space charge profiles of original LDPE and 90°C 5 days aged LDPE, where the effect of the applied voltage and pulse has been removed through data processing, Figure 5 shows that the total injected charge amount of original sample is higher than the amount of 90°C 5 days aged sample, indicating that the lightly aged sample suppresses charge injection.



(a) (b)

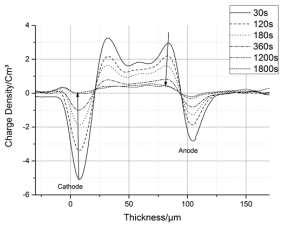
Figure 5: Space charge injection at 40kV/mm for 1800s on original LDPE (a), 90°C 5 days aged LDPE (b).



(a) (b)

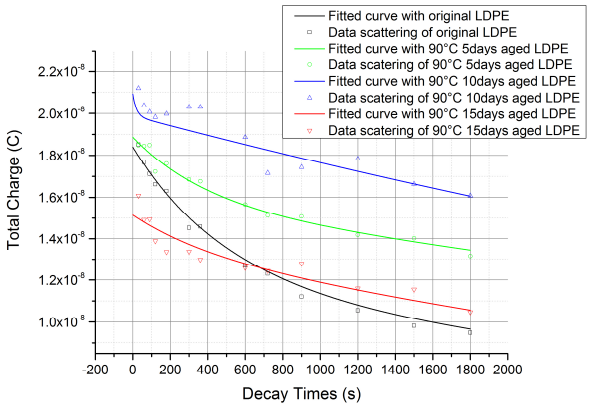
(c) (d)

(e) (f)

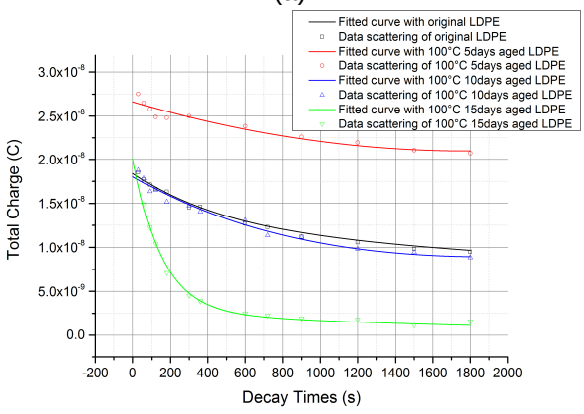


(g)

Figure 6: Space charge decay after the removal of the applied voltage in original LDPE (a), 90°C 5 days aged LDPE (b), 90°C 10 days aged LDPE (c), 90°C 15 days aged LDPE (d), 100°C 5 days aged LDPE (e), 100°C 10 days aged LDPE (f) and 100°C 15 days aged LDPE (g).



(a)



(b)

Figure 7: Curve fitting results of Charge decay after the removal of the applied voltage in original LDPE, 90°C aged LDPE (a) and 100°C aged LDPE (b).

Table 1: The decay time of total charge decay to half of the total decay charge during 1800s.

Decay time (s)	Original	5 days	10 days	15 days
90°C aged LDPE	404	460	653	583
100°C aged LDPE	404	530	480	120

Figure 6 shows space charge decay after the removal of the applied voltage. The exponential decay curves of total charge amount in all the samples are found by using MATLAB curve fitting tool based on equation (3). The total charge of normal and aged samples and its relationship with time is shown in Figure 7. Meanwhile, the first point of each group shows the total charge collected after 30s from the removal of voltage, which is close to the total charge that has been injected into sample after 1800s volts-on. In terms of the fitted curve, the decay time of total charge decay to half of the total decay charge during 1800s can be calculated and shown in Table 1. Generally, it can be observed that the total charge of ageing sample decay with slower rate, compared with the original sample. Exception occurs when the sample was aged for a longer time and higher temperature such as the sample aged at 100°C for 15 days. The charge in the sample aged at 100ºC for 15 days decays rapid initially and the remaining charge decreases with a much slow rate.

Furthermore, Table 1 shows that the decay rate of total charge is rising from original to 90°C 10 days aged sample and from original to 100°C 5 days aged sample but reducing from 90°C 10 days aged sample to 90°C 15 days aged sample and from 100°C 5 days aged sample to 100°C 15 days aged sample, which has the same trend with breakdown strength results as well as the variation tendency of 30s-total charge in decay process that been shown in Figure 7. Meanwhile, it has been observed that the charge peak adjacent to the anode electrode from the aged LDPE sample increases with ageing severity, but the total charge amount inside the sample decreases. This may be due to the recombination effect between positive and negative charges injected from the cathode and anode respectively.

One may be noticed, there is no space charge decay data for the sample aged at 100°C for 20 days. This is because charge decays really fast and nothing is left after15s.

4 DISCUSSTION

In previous paper [11], a universal phenomenon of thermal ageing LDPE has been proposed that the DC breakdown strength of LDPE drops very quickly and its dispersion becomes bigger with the increase of temperature and ageing time in general. While we have shown that the DC breakdown strength slightly increases when it comes to the relatively short time aged sample. Furthermore, the change trend of total-charge-decay rate decreases and the DC breakdown strength is increase in the meantime, which has been shown in Table 1.

From the perspective of chemical change, the FTIR results have shown that thermal ageing in the air leads to a gradual increase in the thermo-oxidative degree of LDPE with the rise of ageing temperature and time. At high temperature, the decrease in electrical breakdown strength is related to changes brought by oxidation, chain scission and crosslinking as well as reduction in crystallinity [10]. From the results of space charge, it seems that more deep traps are introduced into sample during the thermal ageing. However, in the early stage of thermal ageing, an increase in deep trap density means that the captured charges from the injection have difficulty to move around and the electric field produced by the trapped charges hinders further charge injection. Consequently, less charge was observed in the samples aged less. This is a possible reason for increasing breakdown strength observed. Further thermal ageing produces more deep traps, if the number of traps reaches a critical value the probability of charge tunnelling between the two adjacent traps is enhanced. The injected charges now are able to move further into the bulk of the sample. More space charge now can be captured by the sample. As a result, the electric field distortion will be more severe, leading to reduction in breakdown strength. When the sample is severely thermal aged, the charge tunnelling becomes so easy. The conductivity increases and charges become impossible to stay in the bulk after the removal of the applied voltage as evidenced in the sample aged at 100ºC for 20 days. The breakdown strength of such sample will deteriorate significantly.

In terms of the theoretical model based on shallow and deep traps proposed in [2], both the trapping and detrapping procedure of deep trap are slower at the beginning of the whole process. The space charge results have shown that the charge of aged samples injects and decays with a slower rate especially in the vicinity of electrodes. So the primary traps generated in the samples during thermal ageing are deep traps. FTIR results clearly indicate the formation of new chemical groups. And at the beginning of ageing, the thermos-oxidative process just occurs near the surface of sample, so it will bring in a small amount of deep traps. Therefore the region of deep traps can retard the charge injection. This argument is supported by the observation shown in Figure 5.

The total charge decay rate of 90°C 15 days aged sample increases compared with 90°C 10 days aged sample which have the highest breakdown strength in 90°C aged samples, as well as the comparison among 100°C 5 days aged sample, 100°C 10 days aged sample and 100°C 15 days aged sample. As for the samples aged at 100°C for 15 days and 100°C 20 days and 90°C for 15 days, there is a significant chemical change occurring inside of the samples. Huge amount

defects (deep traps) may be generated and charge tunnelling can easily occur. This will lead to a drastic rapid increase in the conductivity, so the charge decays very quickly after the removal of the applied voltage. The results of DC breakdown support this hypothesis, because generally, the higher conductivity can lead to the weaker breakdown strength. The conductivity will be measured in our future work to verify the above hypothesis.

4 CONCLUSIONS

Space charge dynamics in aged LDPE at an applied fields of 40 kV/mm, which were thermally aged at 90 °C for 1, 5, 10 and 15 days and at 100°C for 1, 5, 10, 15 and 20 days in air, have been observed using the PEA technique. In addition, electrical breakdown strength of the aged samples was measured and the data were processed using the Weibull distribution. Following conclusions may be drawn:

(1) Thermal ageing in air leads to a gradual increase in the thermo-oxidative degree of LDPE. The chemical change can generate more deep traps in the samples which influence charge dynamics when subjected to a high electric field.

(2) The trap distribution has a significant impact on breakdown strength. At the early stage of the thermal ageing process, the breakdown strength increases due to the favorable impact of deep traps. The introduction of a small amount of deep traps adjacent to the electrodes can hinder further charge injection. During the sustainable rise of ageing degree, more deep traps are brought into sample, which results in more charges and lower breakdown strength.

ACKNOWLEDGMENT

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